Number/
Numéro

1

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS -PHASE II

FINAL REPORT
PHASE A

DSS FILE NUMBER	26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER	0SQ83-00230
CANMET PROJECT NUMBER	410252

POLLUTECH LIMITED 1090 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1800

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS
PHASE II

Final Report

Phase A

By

POLLUTECH LIMITED

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS FILE NUMBER : 26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER : OSQ83-00230
CANMET PROJECT NUMBER : 410252
CANMET SCIENTIFIC AUTHORITY : Mr. K. Bell

124 pp

March 31, 1985

MICROMEDIA
OCT 11 1985

POLLUTECH LIMITED 1080 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1800

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

The Project Team consisting of staff from Pollutech Limited and the Ontario Research Foundation wish to gratefully acknowledge the assistance provided by the following brick companies, and their staff, in providing samples for analysis for fluoride content:

- Toronto Brick
- Brampton Brick
- Hamilton Brick
- Domtar Construction Material
- Canada Brick
- St. Lawrence Brick
- I-XL Industries
- Citadel Brick
- Clayburn Industries
- L.E. Shaw
- Estevan Brick
- Scott Brick
- Trinity Brick

We also wish to extend an additional thank you to the following plants, and staff, who provided detailed operating data on the production facilities, entertained our many questions during the site visits, and provided bricks and/or raw materials for detailed fluorine evaluation tests:

- I-XL Industries Limited
  Red River Brick & Tile Division
  Winnipeg, Manitoba
- I-XL Industries Limited
  Northwest Brick & Tile Division
  Edmonton, Alberta
- I-XL Industries Limited
  Redcliff Pressed Brick Division
  Redcliff, Alberta
- L.E. Shaw Limited
  Halifax, Nova Scotia
- Citadel Brick Ltd.
  Quebec City, Quebec
- Briqueterie St. Laurent
  LaPrairie, Quebec
- Domtar Construction Materials
  Ottawa, Ontario
- Domtar Construction Materials
  Mississauga, Ontario
- Canada Brick Co. Ltd.
  Streetsville, Ontario
- Canada Brick Co. Ltd.
  Mississauga, Ontario

PHASE II
PROJECT ABSTRACT

- PHASE A

- PHASE B

PHASE II

PROJECT ABSTRACT
PHASE A AND PHASE B

Pollutech Limited have conducted a technical investigation, using additional expertise from the Ontario Research Foundation, in which laboratory scale studies were used to examine means of inhibiting fluoride emissions from tunnel kilns and for brickmaking purposes. The procedures employed were aimed at providing possible alternatives to conventional emission control scrubbers since it was believed, as a result of the Phase I study, that scrubbers would upset thermal balances and result in energy inefficiencies.

The results of the technical investigations are reported separately for Phase A and Phase B of this study. The Phase A report refers specifically to the results of the fluoride analysis on raw materials utilized in Canadian brickmaking plants, the fluoride emission profiles of selected samples under simulated plant conditions, and the development of theorized optimized firing curves for each sample tested. The Phase B report deals with the results of a literature search and experimental program to examine the efficacy of additives and fluxes in inhibiting fluoride evolution from the selected samples.

The results of the **PHASE A** study indicated that:

- the analysis of fluoride in various raw materials from a broad sample of Canadian plants showed fluoride levels ranging from 202 ppm to 1163 ppm, with an average fluoride content of 706 ppm (0.07 percent)
- the variation in fluoride content of the raw materials was related to the geographical area from which the raw material was excavated

- the rate of evolution of fluoride from test brick samples was found to be directly related to the firing temperature, with the most significant fluoride loss at 800°C to 1000°C

- the rate of fluoride evolution varied significantly across the samples tested, ranging from 15 mg/kg-hr to 149 mg/kg-hr, depending on raw material utilized and specific brickmaking practices employed

- in most instances the rate of fluoride evolution is too high to be able to limit the release of fluoride by modification of the firing curve, unless significant reductions in kiln retention time (particularly at the soak temperature), and top firing temperature could be achieved

- gross energy calculations suggest the energy impact of changing the firing sequence is positive (i.e. savings) for those modifications that result in a decrease in fluoride evolution

The results of the **PHASE B** study showed that:

- a review of the literature suggested that a number of additives are available that can be used to limit fluoride evolution by complexing with the fluoride to limit fluoride release upon firing

- the literature also suggested that additives are available that can be added to the raw material, such that the physical properties of the raw material are modified, thereby limiting the release of fluoride

- laboratory testing using the various additives did not appear to have a significant effect on the handling of the raw material or the fabrication of the final product

- the use of additives to complex the fluoride did not result in a significant reduction in fluoride release during firing, and on some occasions fluoride emissions increased

- the use of additives to change the refractory characteristics did not result in a significant reduction in fluoride release during firing

The overall conclusion that can be drawn from the study is that procedures utilizing firing curve control in the **PHASE A** study cannot effectively be given serious consideration for fluoride emission control due to the high rates of fluoride emission and corresponding kiln retention times. The only way the fluoride loss can be decreased is by reducing the total amount of time the brick is exposed to the high temperatures (800°C-1000°C), by a reduction in firing time in conjunction with a reduction in the top firing temperature. This is unlikely to be a satisfactory solution to the problem however, since it would have deleterious effects upon the desired physical properties of the clay brick products so produced. The use of chemical additivies in the **PHASE B** experimental program clearly demonstrates that this alternative does not have a great potential as a solution to fluoride emission control at Canadian brickmaking plants.

POLLUTECH

PHASE A - FINAL REPORT

- Fluoride Content of Raw Materials
- Fluoride Emission Profiles
- Optimized Firing Curves

PHASE A - FINAL REPORT
TABLE OF CONTENTS

Page No.

1. SUMMARY 1
2. PROJECT BACKGROUND 5
   - 2.1 Introduction to Problem 5
   - 2.2 Canadian Clay Brick Manufacturing 8
   - 2.3 Control of Fluoride Emissions By Modification of Firing Schedule 11
3. TECHNICAL WORK PROGRAM 13
   - 3.1 Milestone 1 - Fluoride Content of Raw Materials 13
     - 3.1.1 Sample Preparation Procedures 13
     - 3.1.2 Analytical Procedure 15
   - 3.2 Milestone 2 - Fluoride Emission Profiles 17
     - 3.2.1 Field Visits to Canadian Brick Plants 18
     - 3.2.2 Testing at the Institut Für Ziegelforschung 20
   - 3.3 Milestone 3 - Development of Optimized Firing Curves 22
4. RESULTS OF TECHNICAL STUDY 25
   - 4.1 Fluoride Content of Raw Materials 25
   - 4.2 Plant Operating Data From 10 Canadian Facilities 26
   - 4.3 Fluoride Emission Profiles 28
   - 4.4 Optimized Firing Curves 35
5. CONCLUSIONS & RECOMMENDATIONS 38

TABLES

FIGURES

APPENDICES

SUMMARY

1. SUMMARY

The first phase of the this report was instituted to delineate the thermochemistry of fluoride evolution from typical Canadian clays and to determine the interrelationship betweem current kiln firing practices and idealized theoretical procedures aimed at minimizing fluoride evolution while maintaining or improving energy efficiency. The study involved the analysis of a range of Canadian brickmaking raw materials followed by detailed examination of ten "typical" samples.

The Phase A program was divided into three sub-sections referred to as milestones, each of which were made up of a number of tasks. The milestones were identified as follows:

- Milestone No. 1

  Since there are thirteen companies operating some twenty-three brickmaking plants across the country and since some of these plants utilize more than one raw material type (either singularly or in blends), thirty representative samples of brickmaking raw material from cooperating manufacturers across the country were collected. These were in the form of single constituent clays and shales, or as blends, and were measured for fluoride content. Analysis was carried out using the most up-to-date pyrohydrolysis techniques, and incorporating duplicate samples and pyrohydrolysis of known reference standards.

- Milestone No. 2

  Upon completion of Milestone No. 1, and review of the data, the selection of up to ten typical samples from the initial survey for more detailed examination commenced. Having selected ten representative samples in cooperation with the Scientific Authority all data available to characterize the kiln

profiles used to fire products from the ten selected samples were collected from the cooperating manufacturers. Project staff visited each facility to collect samples and data. A field report for the plants containing all raw material data and kiln operating data was prepared. With this data in hand, samples were forwarded to the Institute Für Ziegelforschung in Essen (West Germany) for determination of the fluoride evolution characteristics. Project staff attended at the German test facility to observe both the evaluations and the test facility.

- Milestone No. 3

Having received the fluoride emission profile data from the Institut Für Ziegelforschung in Essen (West Germany), and having determined the methods for using the information to prepare idealized kiln firing schedules in Milestone No. 2 above, the data were employed to derive theoretical optimized firing curves for each sample tested. The theoretical firing profiles were derived to investigate whether minimum fluoride emissions, based upon the data provided, could be attained while minimizing any energy penalty or preferably maintaining and improving energy consumption.

In order to complete all of the tasks as identified in the three milestones, the project team undertook the following steps:

- contact was made with every known brick plant across Canada to determine whether they were in operation, whether they utilized tunnel kilns, and what their immediate and future production estimates were

- for those plants having sufficient production capacity through a tunnel kiln to be of a regional concern, samples were requested of their raw material and/or raw material mix

- based on a physical examination of the raw material samples, available geological data, and plant location, some 30 samples were selected by the Project Team and Scientific Authority for detailed analysis of fluoride content

- a report on the analytical test results was prepared, and based on the results contained therein, ten plants were selected for detailed review, collection of kiln data, and collection of dried brick samples for further testing of fluoride evolution in a test kiln Essen, West Germany

- staff from the Project Team visited nine of the ten plants from which dried brick samples were collected to document all kiln data and obtain operating data to support the fluoride evolution tests

- dried brick samples were forwarded to the Institute Für Ziegelforschung in Essen, West Germany for determination of fluoride evolution characteristics in a test kiln which applied firing conditions closely resembling those at the full scale plant

- on the basis of the analytical and test results collected, theoretically optimized firing curves were produced and preliminary energy evaluations were made, to determine the energy efficiency of the proposed changes

Completion of all of these tasks in Phase A provided a clear indication of what levels of fluoride could be expected, how much fluoride would be released, and whether the fluoride could possibly be controlled within reasonable energy limits. Specific inferences from this work are as follows:

- the analysis of fluoride in various raw materials from a broad sample of Canadian plants showed fluoride levels ranging from 202 ppm to 1163 ppm, with an average fluoride content of 706 ppm (0.07 percent)

- the variation in fluoride content of the raw materials was related to the geographical area from which the raw material was excavated,

- the rate of evolution of fluoride from test brick samples was found to be directly related to the firing temperature, with the most significant fluoride loss at 800°C to 1000°C

- the rate of fluoride evolution varied significantly among the samples tested, ranging from 15 mg/kg-hr to 149 mg/kg-hr, depending on raw material utilized and specific brickmaking practices employed

- in most instances the rate of fluoride evolution was too high to be able to limit the release of fluoride by modification of the firing curve, unless significant reductions in kiln retention time and top firing temperature could be achieved

- gross energy calculations suggest that the energy impact of changing the firing sequence is positive (i.e. savings) for those modifications which result in a decrease in fluoride evolution

PROJECT BACKGROUND

- Introduction to Problem
- Canadian Clay Brick Manufacturing
- Control of Fluoride Emissions By Modification of Firing Schedule

2. PROJECT BACKGROUND

2.1 Introduction To Problem

While the clay brick manufacturing industry is not generally recognized as a major source of industrial pollution, it has been identified as a significant source of gaseous (and occasionally particulate) fluorides. The fluoride emissions are generated by the action of heat, during the kiln firing process, on fluoride and fluorosilicate minerals closely associated with the clay and shale raw materials used in brick manufacturing.

It is well known that the emission of gaseous and particulate fluoride compounds from industrial sources can present some hazard to the environment by:

- endangering the health of agricultural and foraging animals (and in extreme cases, the health of humans)
- causing damage to vegetation (foliage)
- contributing in general to acid rain

Concern has recently been expressed by the various regulatory agencies over fluoride emissions and it is anticipated that if these agencies seek to control such emissions, some Canadian clay brick manufacturers will be required to reduce the evolution of fluoride compounds from their plants.

The kiln firing operation, which is the major production rate determining operation in the total clay brick manufacturing process, is also the major energy cost source in clay brick manufacturing. Most plants operate on a continuous basis using tunnel kilns which burn fossil fuels. Since the rapid escalation in the cost of oil and gas in the early 1970's, the Canadian clay brick industry has actively worked towards the optimization of its kiln firing operation in order to minimize energy consumption within the manufacturing process. It has been noted that between 1972 and 1981, energy consumption per manufactured unit, within the industry, has decreased by nearly 29 percent. The improvement in efficiency has been obtained by carefully balancing burner operation, load movement through the kiln, air movement through the kiln, and recirculation of both hot combustion gases and cold air to give optimum product quality and minimum fuel usage. Due to the delicate balance and control which has been developed, and is now required to ensure the energy efficient operation of dynamic systems such as tunnel kilns, it is anticipated that the incorporation of conventional emission control measures such as scrubbers could result in a serious reduction of the kiln energy efficiencies achieved in recent years. A major loss in energy efficiency would seriously hamper the industry's ability to compete with other construction materials in the marketplace.

It is essential, therefore, that any measures employed to reduce or control atmospheric emissions are selected on the basis of their possible impact on energy efficiency in addition to their efficacy and reliability as anti-pollution devices. In principle, control of fluoride emissions from tunnel kilns, used for manufacturing clay bricks, can be applied at one of the following three stages in the brickmaking process:

- During selection of raw materials - i.e. select raw materials with a potential for reduced fluoride emission and/or incorporate additives to suppress fluoride evolution.

- During kiln firing process - i.e. alteration of the firing procedure to reduce the rate of fluoride evolution.
- At the gas exhaust stack - i.e. by incorporation of conventional scrubber systems (wet or dry).

The results of the Phase I study by the Clay Brick Association which evaluated installations in Germany suggested that flue gas cleaning systems using conventional wet scrubber technology should only be considered as a last resort due to both major capital operating and running costs, and unreliable performance. A preventative approach through raw material alteration and modification and/or the implementation of changes in the firing process to reduce fluoride evolution at its source appear to be the better alternatives, and therefore the purpose of this study.

Fluoride evolution and fluoride emission control procedures as they relate to the clay brick manufacturing process have been studied in great detail in Europe, particularly in West Germany, and it is clear from published literature that alternative techniques which utilize raw material modification and/or alteration of the firing process are potentially available. Not all European scientists however, agree with this approach.

It is recognized that Canadian manufacturing and kiln-firing technology together with Canadian raw materials differ significantly from those used in Europe. The introduction of these European approaches to North America require significant research on the interrelationship of the thermochemistry of fluoride evolution from Canadian clays and shales with known kiln firing technology and current standard practice. The object of this study was, therefore, to develop guidelines to assist the clay brick industry in selecting energy efficient fluoride control methodology.

2.2 Canadian Clay Brick Manufacturing

The Canadian Clay Brick Industry is made up of thirteen companies operating twenty-three manufacturing plants across the country from Newfoundland to British Columbia. In recent years these companies have collectively manufactured and/or sold in excess of 600 million brick equivalents per year. Typically, the brick making process requires an energy consumption of approximately 5.5 GJ per thousand brick equivalents (5.2×10^6 BTU per thousand brick equivalents).

The manufacturing process for structural clay products typically comprises the following major activities:

- Excavation of raw material - local clays and shales.
- Crushing and grinding to the desired particle size distribution.
- Addition of modifying ingredients - e.g. pigments, barium carbonate for scum control, plasticizers and/or binders.
- Conditioning/tempering with water to produce a suitably plastic mass.
- Forming - by high pressure continuous extrusion through dies of the desired cross-section, followed by cutting to the required size.
- Loading onto kiln cars.
- Drying (in tunnel dryers).
- Firing (in continuous tunnel kilns).
- Unloading, grading, packaging and shipment.

As an impurity in clays and shales, fluorides are widespread. Because fluoride and hydroxyl ions are of nearly equal size and both are monovalent, isomorphous substitution of one for the other can be anticipated in clay mineral structures. In addition, these raw materials also contain many other hydroxyl bearing accessory minerals such as mica, hornblende and apatite, among others, all of which are known to contain strongly-bound fluorine.(1) Coupled with the frequent presence of the mineral fluorspar (CaF_2), these sources provide a potential for fluoride emissions during the ceramic firing cycle.

During the heating stages of the ceramic manufacturing process, the fluoride present in the raw materials is primarily evolved as gaseous hydrogen fluoride (HF) or silicon tetrafluoride (SiF_4), although particulate calcium fluoride (CaF_2) and particulate ammonium fluosilicate(2) $(NH_4)_2SiF_6$ may also be formed when organic impurities are present.

Early estimates of the contribution of the brick industry to the total industrial fluoride emissions were based entirely on laboratory experiments and assumed that all of the available fluoride in the clay or shale was evolved. It has been clearly demonstrated in recent years (3,4) that only a portion of the available fluoride is in fact emitted during the firing operation.

The relative proportion of fluoride evolved is obviously not the same for every clay fired to the same temperature;(1) it will vary with each raw material and with differences in equipment and operational procedures from plant to plant. Fluoride emission occurs during the firing process when the fluorine compounds entrained within the body become thermodynamically unstable. While the presence of water vapour trapped within the firing atmosphere appears to be of prime importance, there are several other important controlling factors, namely: (3,4,5,6,7)

- Firing Cycle- The total firing time, the maximum firing temperature and the dwell time between 800°C and the sintering range of the clay.

- Type of Kiln- Tunnel kilns can be expected to be the source of higher emissions than periodic kilns. The high rate of flow of flue gases, air and humidity over the ware at elevated temperatures increases the rate of removal of fluoride. For example, products in the centre of the kiln charge (hack) will lose less fluoride than those on the outer edges of the kiln car due to temperature gradients and less exposure to high velocity gases.

- Kiln Operating Conditions- The kiln atmosphere, air/fuel ratios, type of fuel, air leakage and the degree of gaseous recirculation will influence the rate and extent of fluoride emissions during firing. Passage of hot gases (by recirculation) over the cooled charge may lead to readsorption of a portion of the evolved fluoride.

- The Degree of Compaction of the Product and Particle Size of the Raw Materials- Denser compacts have been shown to evolve less fluoride than less dense or more porous products. Similarly, finely-ground raw materials yield higher fluoride levels than dense coarse-grained materials. The cross-sectional dimensions of the ware will also influence fluoride emissions.

- Microstructure and Porosity of Product being Fired - Fluoride migration encounters little resistance in porous ceramic materials whereas the presence of densified phases can effectively impede diffusion.

- The Initial Fluoride Content of the Raw Material- Although fluoride emission is not in general stoichiometric, it may be presumed, other conditions being equal, that raw materials high in fluoride content will cause higher levels of emission.

- Calcium Carbonate Content - The presence of finely-divided, naturally occurring $CaCO_3$ in the raw materials has been cited as a factor in limiting the level of fluoride evolution (8).

2.3 Control of Fluoride Emissions by Modification of Firing Schedule

Since the evolution of fluoride from clays and shales is a temperature sensitive reaction, and because the rate of fluoride evolution increases as the operating temperature approaches the vitrification range, it is considered that if the firing temperature of brick products could be lowered significantly it would be possible to not only reduce fluoride emissions but also to conserve energy. Such a reduction in firing temperature could be brought about by the use of fluxes as suggested above.

As an alternative, recent laboratory studies by Tunker and Schmidt(3) and Kother and Pauls (4) on emission rates for fluoride evolution have indicated that modification and control of the kiln temperature profile rather than simple reduction of the firing temperature (particularly in the range of 800°C - 1000°C) may provide a means of reducing and/or controlling fluoride emissions from ceramic plants.

Their studies have shown that the rate of the fluoride emission is not constant with temperature rise. It is dependent upon a number of variables, the most important of which is the concentration of water vapour in the kiln atmosphere. The emission of fluoride is also independent of the total fluoride content of the raw materials (i.e. all of the fluoride is not necessarily emitted during firing). While fluoride evolution commences in the range of 550°C to 750°C, the rate of evolution increases markedly at temperatures greater than 850°C and is completed before the final firing temperature is reached. The cessation of fluoride emission is considered to be due to the onset of vitrification, which seals up the body thus preventing further diffusion of fluoride-bearing gases to the surface.

It has also been noted that because the rate of fluoride evolution is particularly rapid above 850°C, it would be beneficial to heat the products from 850°C to the required final firing temperature as quickly as possible, thereby minimizing the period during which fluoride evolution can occur, and ensuring the rapid onset of vitrification to seal up the pore structure of the product.

Even though such an accelerated heating rate in the region of 850°C to final firing temperature will result in a surge in fuel consumption; the total consumption per unit producton for the entire firing cycle may be reduced due to faster kiln throughputs.

In order to study this phenomenon, samples of Canadian dried bricks were sent to the Institut Für Ziegelforschung in Essen West Germany for evaluation. The dried whole bricks were fired under the same kiln profile conditions as that specified by each plant, and fluoride evolution was monitored.

TECHNICAL WORK PROGRAM

- Milestone 1 - Fluoride Content of Raw Materials
- Milestone 2 - Fluoride Emission Profiles
- Milestone 3 - Development of Optimized Firing Curves

3. TECHNICAL WORK PROGRAM

3.1 Milestone 1 - Fluoride Content of Raw Materials

As a preliminary step in the Phase A program, an initial contact was made with each Canadian brick manufacturer to determine:

- the raw materials utilized,
- the kiln process in use at the plant,
- the production throughput at each facility, and
- whether they wished to participate in the study.

After collection of some 72 raw material samples, the Project Team and the Scientific Authority met to discuss the samples and data collected, and select the 30 samples to be subjected to the raw material fluoride testing. Selection was carried out to provide a good cross-section of Canadian clays and shales, while concentrating on raw materials used in high throughput tunnel kiln operations.

3.1.1. Sample Preparation Procedures

The following samples from Canadian brickmaking plants were subjected to fluoride analysis:

- Brampton Brick, Brampton (Ontario)
- Toronto Brick, Toronto (Ontario)
- Domtar Brick,
    - Mississauga (Ontario)
    - Ottawa (Ontario)
- I-XL - North West Brick & Tile, Edmonton (Alberta)
- I-XL - Redcliff Press Brick, (Alberta)
- I-XL - Medicine Hat Brick & Tile, Medicine Hat (Alberta)
- I-XL - Medicine Hat Sewer Pipe, Medicine Hat (Alberta)

- I-XL - Red River Brick & Tile, Winnipeg (Manitoba)
- I-XL - Western Clay, Regina (Saskatchewan)
- Canada Brick, Streetsville (Ontario)
- Canada Brick , Burlington (Ontario)
- Citadel Brick Ltd., Ste. Anne (Quebec)
- Clayburn Industries Ltd., Abbotsford (British Columbia)
- L.E. Shaw Ltd., Halifax (Nova Scotia)
- Estevan Brick, Estevan (Saskatchewan)
- St. Lawrence Brick Co. Ltd., La Prairie (Quebec)
- Trinity Brick Products, St. John's (Newfoundland)

All samples, upon arrival at Pollutech's Oakville laboratory, were tagged for future identification. A code number was assigned for identification of the sample and a separate laboratory code was assigned to ensure confidentiality of all data. All sample results reported herein are by laboratory code only, which is independent of the source of the raw material.

The raw material samples were dried at 45°C to remove excess moisture and promote particle separation. Larger clay materials were reduced in size using a mechanical grinder. The subsequent bulk powdered samples were split using a chute riffler. This was then followed by a more precise rotary riffling to supply a small representative sample for the pyrohydrolysis stage. Typically, a 10 gram sample was prepared by the riffling procedure.

The riffled sample was further ground to 200 mesh (ASTM) or less using an Agate Mortar (fluoride free). A 100 mg sample containing 0.1 to 4 mg of fluoride was weighed out. Approximately 250 mg of the catalyst (Vanadium pentoxide) was also weighed out. The 100 mg sample was ground with one-third of the vanadium pentoxide in the agate mortar, and this was then transferred to a quartz combustion boat. The remainder of the sample was extracted from the mortar by grinding with the Vanadium Pentoxide in two portions.

3.1.2 Analytical Procedure

The pyrohydrolysis apparatus, as depicted schematically in Figure 1, generates the concentrate for the follow-up fluoride analysis and consists of the following major components:

- quartz tube furnace
- steam generator
- air supply
- condensor tube
- sample collector

To start the procedure the condenser was connected to the tube furnace exhaust for the collection of the steam condensate. A polyethylene bottle containing 5 ml of the alkaline absorbent solution was placed at the end of the condenser, with the end of the tube submerged. The quartz tube furnace was then preheated to 400°C.

The quartz combustion boat and sample, as previously prepared in accordance with Section 3.1.1, was placed at the mid point of the tube furnace. The temperature at this point had previously been checked by a rod thermocouple. The steam generator was then started and the tube furnace temperature was increased to 850°C. The system was maintained in this state until 200 mls of condensate had been collected. On average this step took 100 minutes. Duplicate pyrohydrolysis reactions were carried out on each sample analysed.

After collection of the first 200 mls of condensate, the air supply was turned on to collect the few final drops of condensate. The steam generator was then disconnected, and the sample boat was removed. At this point the furnace was turned down to 400°C and the steam generator was reconnected with the clean air purge. This cleaning process continued until the temperature had dropped to 400°C, this took a period of approximately 30 minutes.

The concentration of fluoride in the condensate sample was determined by standard procedures utilizing an ion-selective electrode. The electrode was calibrated against a standard reference solution, prepared by serial dilution to 0.1 mg/L, 1.0 mg/L and 10 mg/L. An equal part of ISA/pH buffer was added to each standard. When the electrode was placed in the mid-range solution of 1.0 mg/L the meter was calibrated after 3 minutes of stirring. Following this the electrode was placed in the 10 mg/L standard, and after 3 minutes of stirring the temperature compensation was adjusted to give a full-scale reading. The meter was therefore set to read 0.1 mg/L to 10 mg/L directly.

Each condensate sample was treated with an equal part of the ISA/pH buffer, and thereafter the mg/L fluoride was determined by direct readout from the meter. This value was then used to determine the fluoride content on a weight ppm basis (mg/kg) as follows:

$$\text{mg/L fluoride} \times \frac{250\text{ mL sample}}{1000\text{ mL}} \times \frac{1{,}000{,}000\text{ mg/kg}}{100\text{ mg sample}} = \text{mg/kg Fl}^{-}\text{(ppm)}$$

Several steps were taken by Pollutech's analytical staff to ensure that the fluoride results were accurate. Quality control procedures were utilized throughout the pyrohydrolysis/analysis stage as follows:

- duplicate tests were run on all samples including both the pyrohydrolysis and ion selective electrode analysis
- two (2) known standards were subjected to the test procedure, on multiple occasions, and all results were within plus or minus 5%
    - NBS standard #91 : Opal Glass
    - NBS standard #1206 : Phosphate Rock

- know weights of sodium fluoride (NaF) were run through the pyrohydrolysis procedure, and additional known concentrations of NaF were used to verify the ion-selective electrode procedure

- combustion boats were run through the pyrohydrolysis procedure empty and showed no fluoride

- combustion boats were re-fired in the pyrohydrolysis system after the preliminary test and no fluoride residual was detected

- two operators ran duplicate samples and achieved identical results on numerous occasions

In general the pyrohydrolysis plus ion-selective electrode procedure was found to be very stable. Any variation in fluoride content between these results and those reported elsewhere would be more likely dependent on sample collection or other methods of fluoride analysis.

3.2 Milestone 2 - Fluoride Emission Profiles

This part of the project entailed selection of ten typical samples, from the thirty analysed, for detailed study on the evolution of fluoride during the kiln firing process. The first task of Milestone 2 was to collect all the applicable data on the plants to be studied, plus collection of dried brick samples for further testing at the Institut Für Ziegelforschung.

3.2.1 Field Visits to Canadian Brick Plants

Project Team members contacted each of the ten plants to arrange for the necessary data and samples. Plant visits documented all of the operating technology at nine specific plants so as to provide as much information as possible to the German scientists conducting the emission profiles.

The following information was requested and studied in relation to fluoride emission:

- Typical chemical analysis of raw materials.
- Time/temperature kiln profiles (where available, data from travelling thermocouple runs were used).
- Production tonnage/fuel consumption, and type of kiln and fuel used. (i.e. top fire or side fired kiln, gas, oil or solid fuel).
- Kiln atmosphere profiles in the various zones of the kiln, insofar as they are known (including any oxidants or reductants added to the kiln atmosphere).
- Product test data (i.e. physical property measurements) on typical products to indicate overall firing effectiveness on microstructure development (i.e. absorption properties, porosity and compressive strength).

While at each plant site the Project Team met with the appropriate representatives with an aim to:

- outline the purpose of this study and explain how the results will help the industry on the whole.
- discuss the production tonnage/fuel consumption data at the plant and its relation to the kiln used, and how much variability is available,
- review the details of the brick manufacturing processes used at each individual plant, from raw material mining through to final product packaging, and
- collect representative dried brick samples for future test work in Germany.

The three samples selected by the Scientific Authority to represent Western Canada production all originated from plants operated by I-XL Industries Limited (head office in Medicine Hat, Alberta). The specific three plants visited were as follows:

- Red River Brick and Tile Division
  Winnipeg, Manitoba

- Northwest Brick and Tile Division
  Edmonton, Alberta

- Redcliff Pressed Brick Division
  Redcliff, Alberta

The seven samples selected by the Scientific Authority to represent Eastern and Central Canada production originated from plants operated by:

- L.E. Shaw Limited
  Halifax, Nova Scotia

- Citadel Brick Ltd.
  Quebec City, Quebec

- St. Lawrence Brick
  La Prairie, Quebec

- Domtar Construction Materials
  Ottawa, Ontario

- Canada Brick Co. Ltd.
  Streetsville, Ontario

- Canada Brick Co. Ltd.
  Burlington, Ontario

- Domtar Construction Materials
  Mississauga, Ontario

3.2.2 Testing at the Institut Für Ziegelforschung

Upon collection of the ten specific samples for fluoride evolution analysis, the samples were shipped to Essen, West Germany. Specific plant data (firing curves) were made available to the German research staff prior to receipt of the samples. Additional data on the raw materials, production process utilized, additives, fuel consumption, etc. was taken to Germany by the Project Team member.

The information gathered by this analytical technique not only monitored fluoride evolution from the clay brick formulations as a function of temperature rise, but also identified specific temperature ranges during which the fluoride evolution rate was at its maximum and the point where microstructural changes (glass formation) began to inhibit the evolution. The data generated indicated those portions of the firing schedule which require changes or more control, if alteration of the firing process is to be used as a means of minimizing fluoride emissions.

The test system utilized at Essen consisted of an INCONEL 600 lined muffle furnace, coupled to a BRAN & LUBBE SENSIMETER G fluoride analyser. A summary of the system and its operation is as follows:

- the muffle furnace is closed at one end and fitted with a gas exhaust and air sampling train

- the furnace is packed with Inconel boxes to reduce the firing space to about 1 cubic meter

- the furnace has 3 separately controlled electric windings to ensure temperature uniformity in the cental zone

- the furnace temperature control was provided via a cam which was cut to match the actual kiln operating data

- air is pumped into the furnace at about 0.88 cubic meter per hour

- water is injected directly into the furnace to achieve the desired kiln moisture content (approximately 3 percent in this case)

- gaseous emissions are collected continuously and analysed automatically every 6 minutes by the specific ion electrode procedure

- the analytical signal from the specific ion electrode is stored in a microcomputer together with temperature information and the data manipulated to provide the characteristic curves

3.3 Milestone 3 - Development of Optimized Firing Curves

Utilizing the technical data derived from the fluoride emission profiles, in conjunction with existing data on the specific plant kiln profiles, the Project Team undertook to develop theoretical optimized firing curves for each sample tested. The firing curves were developed with due regard given to:

- the flexibility available in the kilns at the plants studied,

- the limitations suggested on the effect of any firing changes on the final product quality,

- any energy penalties or benefits associated with the proposed kiln firing schedule modifications.

The modified firing curves were developed after consultation with staff from the Clay Brick Association of Canada Fluoride Sub-committee and the Scientific Authority. Preliminary data suggested that only maximum firing rates and/or shorter kiln retention times could provide the results required. The modified firing curves took into account the "ultimate" firing temperature, so as to review whether a reduction in the firing temperature resulted in an overall reduction in fluoride evolution. Additionally, the rate at which the kiln fired from 850°C to the peak firing temperature was evaluated, with specific emphasis on expected ceramic changes.

Utilizing the modified firing curves the Project Team evaluated the change in fluoride emissions and the energy impact of such a change. For evaluation of "gross" energy changes, an evaluation of all firing curves was made to determine the energy requirements in "degree-hours", which represents the total heat in the kiln temperature profile. This evaluation was extended to include both the energy involved in attaining peak temperatures, and the total energy for the complete kiln process. The expected total fluoride emissions were calculated on the basis of the fluoride emission rate for the mean temperature during each step in the kiln firing process.

In the evaluation of the energy changes due consideration was given to the following:

- the total energy requirements estimated by using degree-hours for the existing firing curve during heating and cooling, for both theoretical and actual kiln operation

- additional energy needs to move from 850°C to firing temperature quickly so as to limit the time at which maximum fluoride release is occurring

- energy savings during cool-down if the total firing time remained constant and heat is recovered

- energy savings during cool-down if the total firing time can be reduced by this procedure and heat is recovered

From the existing plant data calculations were also made to estimate the theoretical energy requirements to fire the bricks, without delving into great detail on the detailed chemistry involved. This estimate was then compared to the energy needs given by plant staff to determine a gross efficiency factor. Both the computed and actual energy needs were used to determine the kiln energy rating, so as to indicate the energy input to achieve the given degree-hours shown by the kiln profile.

As a final step in this milestone, consideration was given to the efficacy of installing additional burners, or other associated equipment, to reach the required firing conditions. This part of the project relied on input from the plant staff involved in the kiln operation.

RESULTS OF TECHNICAL STUDY

- Fluoride Content of Raw Materials
- Plant Operating Data From Ten Canadian Facilities
- Fluoride Emission Profiles
- Optimized Firing Curves

4. RESULTS OF TECHNICAL STUDY

4.1 Fluoride Content of Raw Materials

As previously indicated, the raw material samples were coded to protect the confidentiality of the specific brick manufacturers. The code for the identification of the individual samples is known only by the Scientific Authority and senior Pollutech staff. The reporting of individual results to the manufacturers is through the office of the Scientific Authority only.

The lab test results are given in the attached Table 1, which shows the result for both pyrohydrolysis runs and the corresponding average fluoride content of the material analysed.

The average fluoride content of the raw brick-making material across Canada was found to be 706 ppm, with a peak level of 1163 ppm and a minimum level of 202 ppm.

On a percent-of-occurrence basis the following summary table outlines the range of levels found for fluoride in the raw material:

Fluoride Levels ppm	Percent of Samples in Range
0-200	0
201-400	10.0
401-600	20.0
601-800	36.6
801-1000	20.0
1001-1200	13.4
1201-1400	0

RE: Phase A - Report Section 4.1

As requested, the following identifies the geographical areas referred to in our Phase A Final Report:

Area	Provinces Included	No. Of Samples
1	British Columbia	2
2	Alberta	5
3	Saskatchewan	4
4	Manitoba	4
5	Ontario	7
6	Quebec	3
7	Maritimes	5

Please note that these are geographical areas only and were not selected to represent geological formations.

On a regional basis there is a definite trend in the fluoride content of the raw materials analysed. Although we are unable to report the actual level for each plant due to project confidentiality, we can safely classify results in terms of geographical areas as follows:

Area	Average Fluoride Level (ppm)
1	335
2	484
3	585
4	626
5	660
6	929
7	1000

4.2 Plant Operating Data From 10 Canadian Facilities

The data collection of raw material characteristics, final product characteristics, and fuel consumption is presented in Appendix 2 for each of the ten operating plants visited. Information collected on equipment in use, product mix, and product has not been reported so as not to reveal information which could inadvertently release confidential data. Accordingly the plants have been coded alphabetically, and without correlation to the fluoride data or kiln profiles. The Scientific Authority is in possession of all data relating all factors. The detailed firing curves for each of the ten plant's samples are given in Figures 2 to 11.

The detailed plant data clearly indicates the wide variation in the Canadian brick plants evaluated as part of this study. For the 10 plants evaluated the following summary points are noted:

- typical kiln retention times ranged from 26 hours to 72 hours
- actual plant production varied from 112 metric ton/day to 327 metric ton/day
- fuel consumption data showed energy variations for 2.1 GJ/metric ton (911 BUT/lb) to 4.7 GJ/metric ton (2000 BTU/lb)
- chemical composition of the raw material varied between 22 to 70 percent SiO_2 with anywhere from 0.3 to 7 percent lime
- physical properties data of the fired ware showed fluctuations in compressive strength from 5000 PSI to 14,000 PSI, with C/B ratios from 0.6 to 0.84

Individual plant operations have been detailed in the site visit reports, copies of which have been provided for the Scientific Authority and the individual plant staff (specific plant data only). These reports detail all production equipment utilized in the process.

4.3 Fluoride Emission Profiles

The fluoride emission profiles received from the Institute Für Ziegelforschung provided details on the total fluoride evolution and the rates of fluoride evolution for each of the ten samples submitted. The data received is as depicted in Figures 12 to 21. The rate of fluoride emissions has been standardized relative to kiln temperature for comparative purposes. This data is illustrated by Figures 22 to 31.

In summary the figures show:

- there is a wide fluctuation in the rates of fluoride emission, the total mass of fluoride emitted, and the point of maximum fluoride emission
- the fluoride emission rates range from 15 mg/kg-hr to 149 mg/kg-hr, depending on the raw material utilized and the brickmaking procedure employed
- the total mass of fluoride released is dependent on the maximum rate of fluoride release
- a significant fraction of the fluoride is released after the peak firing temperature is achieved, suggesting that either the fluoride is not "locked-in" by the process or "wash-out" is occurring from the test kiln
- the total amount of fluoride released form the bricks ranges from 15 to 96 percent of the green brick content, with an average of 57 percent fluoride loss

A summary of the fluoride release data for the various samples showing maximum release rates and temperatures at which these occur is as follows:

Plant Code	Kiln Retention (hours)	Maximum Fluoride Release		
		(deg C)	(mg/kg-hr)	(%)
100	40	1040	76	54
102	72	1000	15	86
103	42	1040	149	90
104	29	1010	32	15
105	55	1010	32	31
107	50	950	81	50
108	26	1010	51	37
109	26	1020	104	55
110	46	1010	86	96
111	48	1000	86	58

The fluoride emission profiles agree in principle with the data reported in the literature, that is fluoride release maximizes between 800°C and 1000°C. The results also confirm that fluoride emissions decrease in rate prior to reaching peak temperatures.

Our interpretation of this specific data varies somewhat from that reported by the German Scientific Group, in that we cannot specifically state that the onset of sintering results in a fluoride emission rate reduction. On a purely chemical reaction basis, one would expect the rate of fluoride emission to decrease with a decrease in the remaining fluoride in the brick structure. The data indicates that in most cases, the high rates of fluoride evolution would result in near exhaustion of fluoride in the samples prior to reaching the peak firing temperature. Residual fluoride evolved after this time may in fact represent fluoride washout from the test furnace. The onset of sintering and the reduction in the fluoride emission rate are therefore probably coincidental.

Interpretation of the German data on the same basis as that reported in the literature is confounded by the results shown in Figure 29 for Sample #109. This is the only duplicate run, and was carried out due to a temperature inconsistency in the first run. When the second run was completed, which was identical except for a 30°C - 50°C temperature increase, the fluoride emission results were significantly different. The rates of fluoride emission for the two runs reported were:

	Fluoride Emission (mg/kg-hr)	
Temperature (°C)	Low Run 1	High Run 2
750	1.5	4.7
800	2.9	7.2
850	6.6	13.7
900	13.8	28.9
950	27.7	75.4
1000	44.5	95.6
1010	44.5	103.6

It is our belief that given the same conditions except for temperature, the actual rate of fluoride emission for a given temperature on the curve should be constant. In this case the results vary by as much as 200 percent. We would have expected some sampling variation, and a new peak rate at the peak temperature, but all other data should have been similar. There is no technical explanation why 75 mg/kg-hour fluoride was emitted at 950°C in Run 2, while only 28 mg/kg-hour was emitted at 950°C during Run 1.

All of the fluoride evolutions were modelled on the basis of actual test results for each specific sample. In all cases the fluoride evolution rates, as depicted in Figures 22 to 31, were definable by a power curve rate reaction of the form:

Fluoride Emission
Rate (mg/kg-hr) = α (Temperature -°C)$^{\beta}$

α Range = 3.86×10^{-54} to 4.77×10^{-17}
β Range = 5.85 to 18.55

Each green brick generated a specific set of constants for the model, and these were used to predict fluoride loss under all of the conditions evaluated. Limits placed on the rate reaction were based on actual German test results (i.e. maximum total fluoride release).

Duplicate tests on Sample #109, as illustreated by Figure 19 and Figure 29, demonstrates two different fluoride release rates for the same sample. All conditions except temperature level attained were reported as constant (note 0.2 percent moisture variation).

Projected fluoride emission data for each sample using the rate data and each option evaluated are presented in Tables 3 to 12. Fluroide evolution is shown in terms of:

- emission rates (mg/kg-hr)
- fluoride evolved during each temperature period
- total fluoride release, and
- time/temperature at which point all of the fluoride has left the brick structure

Specific attention should be paid to sample #109 in Table 10 (two runs) which demonstrates test condition effects.

If the rates of fluoride emission are so drastically different for a specific sample at a fixed temperature, then modelling of the results would be impossible. Any interpretations made that assumed emission rates were highly temperature dependent would also be questionable.

4.4 Optimized Firing Curves

Optimized firing curves for each of the ten samples tested were prepared, based on moving through the maximum fluoride evolution period at a faster rate with and without a reduction in kiln retention time. The proposed firing curves are outlined in Figures 32 to 41. Each graph of kiln temperature versus time shows the following:

- a proposed firing curve in which the rate of heating from 850°C to top kiln temperature has been increased, without any further changes in the kiln operation (Option A)

- the proposed curve with a greater heating rate and corresponding shorter kiln retention time (Option B)

The energy analysis for the existing kiln profile for each sample is detailed in Table 2. This information forms the basis upon which energy impacts from proposed kiln firing curve changes was determined. The total energy of the kiln curve was determined using a "SUMMAGRAPHICS BIT PAD ONE" computerized planimeter, giving degree-hours with variation of approximately 1.15 percent.

Utilizing the same procedure as used for the existing kiln profile, the total energy of each modified profile was determined. From this evaluation the following summary table of net requirements was developed:

Plant Code	Existing Energy (Degree-Hours)	Modified Energy (Degree-Hours) Opt.A	Opt.B	Energy Savings (Percent) Opt.A	Opt.B
100	25,370	22,852	20,032	10	21
102	53,510	46,213	44,528	14	17
103	28,150	25,621	25,037	9	11
104	17,010	15,074	14,623	11	14
105	35,360	26,656	29,123	25	18
107	27,880	24,784	25,447	11	9
108	17,510	15,439	14,810	12	15
109	17,380	16,073	16,239	8	7
110	35,150	30,768	29,924	12	15
111	30,890	24,509	21,744	21	30

Detailed calculations for each of the ten samples showing the fluoride evolved during each period in the kiln are presented in Tables 3 through 12. This data indicates at which point the total fluoride content of the sample brick was evolved, for the 3 conditions (normal, faster rate, reduced time). A summary table of this data is as follows:

Calculated Average Fluoride Release (%)

	To Firing	Total
Normal	93	100
Option A	77	95
Option B	86	95

The percent fluoride released is shown for NORMAL (existing kiln conditions), OPTION A (faster firing rate, same retention time) and OPTION B (faster rate, faster time). In all cases the total average fluoride release results in less than a 5 percent reduction in fluoride emissions due to the high rates of release experienced. On an individual sample basis 50 percent of the samples were not affected by the modified firing procedures, and of the remaining never more than a 49 percent reduction in fluoride release could be achieved. The detailed results for each sample are given in Table 13.

The final report received from the researchers in Germany stated "that on the basis of the two runs on sample #109, a reduction of about 30 - 50°C can lead to a 50 percent reduction in fluoride emissions". Assuming this to be a true statement, the data for samples #100 and #103 were re-evaluated with a 50°C overall temperature reduction. This data is shown in Figures 42, 43, and 44 for sample #100 where the model shows net reduction was achieved. The 50°C temperature drop did not affect the end result for sample #103.

Based on an evaluation of the modified firing schedules from both the standpoint of energy demand and fluoride release it becomes apparent that although there is a positive energy benefit, the decrease in fluoride released is insufficient to warrant full-scale application of the procedure, unless an overall reduction in firing temperature can be achieved. Even then only some samples show a net reduction in fluoride loss, and this final level may not be adequate from an environmental standpoint.

Our concerns regarding the interpretation of the data, as outlined in Section 4.3, also impact greatly on this evaluation. There is a lack of evidence to support the conclusions which suggest that the observed changes are "true" changes.

PHASE A

CONCLUSIONS AND RECOMMENDATIONS

5. CONCLUSIONS & RECOMMENDATIONS

The major objectives of Phase A of this project were to:

- determine the fluoride variation in clay brick raw materials across Canada
- determine the fluoride emission rates from selected green brick samples, and
- evaluate the efficacy of modifying kiln firing schedules to control fluoride emissions

Conclusions that can be drawn on the basis of the Phase A results are as follows:

- the level of fluoride in clay brick raw material varies in the different areas across Canada, ranging from a low of 0.02 percent to a high of 0.11 percent, with an average of 0.07 percent
- the maximum rate at which fluoride is evolved from the green brick ranges from 15 mg/kg-hr to 149 mg/kg-hr, resulting in 15 percent to 96 percent fluoride loss
- the samples with the greatest fluoride emission rate lost the greatest mass of fluoride, and
- for the high fluoride rates encountered, the kiln retention times are too long to enable any significant reduction in fluoride release to be achieved by modifications to the kiln firing schedule.

Based on the results to date it would not appear practical to continue with any planned full-scale testing of kiln modifications until the following points have been covered:

- samples of green brick should be fired under under a series of the proposed modified kiln procedures to determine whether the projected fluoride release is achieved,
- the test kiln procedure utilized in Germany must be evaluated in detail from the chemical reactor standpoint to determine whether observed results are dependent on kiln design rather than actual fluoride release mechanism,
- representative samples of raw and fired brick should be collected from the ten participants to determine the true loss of fluoride across the kiln, in comparison to that found in the bench-scale German tests, and
- stack sampling should be carried out on a few select plants to enable development of a true fluoride balance.

Of most importance the work concluded to date has:

- provided a good starting data base for fluoride levels in Canadian raw materials,
- pinpointed the areas where fluoride atmospheric emissions would be at a maximum, and
- demonstrated that European technology is not directly transferable to provide a Canadian solution until such time as inconsistencies in the tests results are evaluated.

This program has however, allowed for review of a German technology, which can now be implemented in Canada, after modification. This will allow for continuing research in this particular area with greater technical assurance, at a reduced expense and with greater Canadian content.

TABLES

TABLE 1: RESULTS OF FLUORIDE ANALYSIS ON SELECTED RAW MATERIALS

Sample Code	Flourine Content (mg/kg) Test 1	Test 2	Average
2	750	800	775
3	700	688	694
11	950	1025	988
12	1125	1025	1075
15	500	520	510
17	205	198	202
18	650	600	625
19	1050	925	988
21	500	450	475
22	1075	1050	1063
26	725	725	725
27	1000	1025	1013
33	675	725	700
36	700	725	713
37	725	725	725
43	425	425	425
46	388	383	386
48	850	925	888
51	1175	1150	1163
56	400	425	413
59	438	423	431
61	925	925	925
67	450	475	463
68	613	650	632
70	900	913	907
76	263	250	257
82	700	700	700
83	725	700	713
86	975	1000	988
96	623	603	613
AVERAGE	706	705	706
MAXIMUM	1175	1150	1163
MINIMUM	205	198	202

ENERGY DEMAND FROM COMPUTERIZED PLANIMETER ANALYSIS
OF EXISTING KILN FIRING CURVES

CONSTANTS:

brick weight (kg)	1.90
specific heat	0.22
specific gravity	1.50
KJ/kg-deg C	0.33

MPLE #	ENERGY AS DEGREE-HOURS to firing temp	after firing	total kiln	KILN FIRING fire deg C	start deg C	total hours	ENERGY USED BTU/lb	GJ/tonne	KILN LOAD ton/day	tonne/day	total tonne	ENERGY RELATED TO KILN HOLDUP theory GJ	actual GJ	efficiency %	KILN ENERGY RATING KJ/deg-hour theory	actual
100	16280	9090	25370	1038	371	48	911	2.12	248	225	375	346	795	43	13622	31317
102	29370	24140	53510	1075	210	72	1300	3.02	170	154	463	553	1399	40	10334	26143
103	15300	12850	28150	1079	343	42	1000	2.33	360	327	572	581	1329	44	20648	47222
104	9700	7310	17010	1038	149	29	901	2.28	235	213	258	316	588	54	18583	34554
105	21880	13480	35360	1038	177	55	2000	4.65	172	156	358	425	1663	26	12031	47041
107	21330	6550	27880	982	371	50	990	2.3	165	150	312	263	718	37	9443	25755
108	11860	5650	17510	1043	284	26	1100	2.56	250	227	246	285	630	45	16276	35979
109	11700	5600	17300	1049	284	26	1050	2.44	200	181	196	229	478	48	13176	27582
110	27940	7210	35150	1077	399	46	1700	3.95	123	112	214	200	846	24	5700	24058
111	22440	8450	30890	1049	260	48	1350	3.14	252	229	457	498	1436	35	16137	46476

TABLE 2

EFFECT OF KILN CHARGE ON RATE
SAMPLE 100 AT GIVEN FLUORIDE RATE

TIME						MID TEMPERATURE (C)						RATE (mg/kg-hr)			PERIOD RELEASE (mg/kg)			TOTAL RELEASE (mg/kg)		
START	END	ELAPSE	LOW	HIGH	NORM	LOW	HIGH	OPT A	LOW	HIGH	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B
0	10	2	371	460	420	371	490	431	371	420	396	0	0	0	0	0	0	0	0	0
10	13	3	460	593	531	490	530	510	420	550	485	0	0	0	0	0	0	0	0	0
13	15	2	593	732	663	530	550	540	550	700	625	0	0	0	1	0	0	1	0	1
15	17	2	732	857	795	550	590	570	700	850	775	4	0	3	8	0	6	9	0	6
17	19	2	857	927	892	590	690	640	850	1024	937	15	0	27	31	1	55	40	1	61
19	22	3	927	996	962	690	996	843	1024	1030	1031	37	0	84	111	24	252	151	25	314
22	24	2	996	1024	1010	996	1024	1010	1030	1010	1024	66	66	78	132	132	155	283	157	469
24	26	2	1024	1030	1031	1024	1030	1031	1010	843	927	84	84	24	168	168	48	452	325	517
26	28	2	1030	1010	1024	1030	1010	1024	843	732	788	78	78	4	155	155	7	607	481	524
28	30	2	1010	843	927	1010	843	927	732	649	691	24	24	1	48	48	2	628	529	526
30	33	3	843	732	788	843	732	788	649	496	573	4	4	0	11	11	0	628	539	526
33	34	1	732	649	691	732	649	691	496	274	385	1	1	0	1	1	0	628	540	526
34	37	3	649	496	573	649	496	573	274	274	274	0	0	0	0	0	0	628	540	526
37	39	2	496	274	385	496	274	385	274			0	0	0	0	0		628	540	526
39	40	1	274	274	274	274	274	274				0	0	0	0	0		628	540	526

TABLE 3

EFFECT OF KILN CHANGE ON RATE
SAMPLE 102 AT GIVEN FLUORIDE RATE

	TIME					MID TEMPERATURE (C)						RATE (mg/kg-hr)			PERIOD RELEASE (mg/kg)			TOTAL RELEASE (mg/kg)		
START	END	ELAPSE	LOW	HIGH	NORM	LOW	HIGH	OPT A	LOW	HIGH	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B
7	10	3	210	415	313	210	240	225	210	350	280	0	0	0	0	0	0	0	0	0
10	13	3	415	515	465	240	270	255	350	500	425	0	0	0	1	0	0	1	0	0
13	16	3	515	620	560	270	330	300	500	650	575	1	0	1	2	0	2	2	0	2
16	20	4	620	725	673	330	375	353	650	850	750	2	0	3	7	0	13	9	0	15
20	23	3	725	800	763	375	450	413	850	1005	928	3	0	11	10	0	32	19	1	47
23	26	3	800	875	838	450	550	500	1005	1050	1028	6	0	20	10	1	59	37	1	106
26	29	3	875	950	913	550	750	650	1050	1045	1048	10	1	22	30	4	66	67	5	173
29	33	4	950	1005	978	750	1005	878	1045	1075	1060	15	0	24	59	31	95	126	37	267
33	36	3	1005	1050	1028	1005	1050	1028	1075	1010	1043	20	20	21	59	59	64	185	96	286
36	39	3	1050	1045	1048	1050	1045	1048	1010	935	973	22	22	14	66	66	43	251	162	286
39	43	4	1045	1075	1060	1045	1075	1060	935	850	893	24	24	9	95	95	35	286	257	286
43	46	3	1075	1010	1043	1075	1010	1043	850	805	828	21	21	6	64	64	17	286	286	286
46	49	3	1010	935	973	1010	935	973	805	750	778	14	14	4	43	43	12	286	286	286
49	52	3	935	850	893	935	850	893	750	700	725	9	9	3	26	26		286	286	286
52	56	4	850	805	828	850	805	828	700	650	675	6	6	2	22	22		286	286	286
56	59	3	805	750	778	805	750	778	650	645	648	4	4	1				286	286	286
59	62	3	750	700	725	750	700	725	645	605	625	0	0	1				286	286	286
62	65	3	700	650	675	700	650	675	605	605	605	0	0	1				286	286	286
65	69	4	650	645	648	650	645	648				0	0					286	286	286
69	72	3	645	605	625	645	605	625				0	0					286	286	286

TABLE 4

EFFECT OF KILN CHANGE ON RATE
SAMPLE 103 AT GIVEN FLUORIDE RATE

	TIME					MID TEMPERATURE (C)						RATE (mg/kg-hr)			PERIOD RELEASE (mg/kg)			TOTAL RELEASE (mg/kg)		
START	END	ELAPSE	LOW	HIGH	NORM	LOW	HIGH	OPT A	LOW	HIGH	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B
3	6	3	343	654	499	343	240	292	343	350	347	0	0	0	0	0	0	0	0	0
6	8	2	654	735	695	450	450	450	450	500	475	0	0	0	1	0	0	1	0	0
8	11	3	735	799	767	500	500	500	550	650	600	2	0	0	6	0	0	7	0	0
11	14	3	799	913	856	550	550	550	750	850	800	8	0	3	25	0	10	32	0	10
14	18	4	913	1074	994	720	720	720	1074	1005	1040	65	1	122	262	3	487	294	3	497
18	21	3	1074	1079	1077	1074	1074	1074	1079	1050	1065	197	191	169	590	572	506	620	575	620
21	23	2	1079	1046	1063	1079	1079	1079	1046	1045	1046	164	203	132	329	406	264	620	620	620
23	24	1	1046	999	1023	1046	1046	1046	999	1075	1037	97	133	118	97	133	118	620	620	620
24	27	3	999	777	888	999	999	999	777	1010	894	14	71	15	42	212	46	620	620	620
27	29	2	777	652	715	777	777	777	652	935	794	1	2	3	1	4	6	620	620	620
29	32	3	652	596	624	652	652	652	596	850	723	0	0	1	0	1	3	620	620	620
32	34	2	596	538	567	596	596	596	538	805	672	0	0	0	0	0	1	620	620	620
34	38	4	538	438	488	538	538	538	438	750	594	0	0	0	0	0	0	620	620	620
38	40	2	438	218	328	438	218	328				0	0	0	0	0		620	620	

TABLE 5

EFFECT OF KILN CHANGE ON RATE
SAMPLE 104 AT GIVEN FLUORIDE RATE

TIME START	TIME END	TIME ELAPSE	LOW	HIGH	NORM	MID TEMPERATURE (C) LOW	MID TEMPERATURE (C) HIGH	MID TEMPERATURE (C) OPT A	LOW	HIGH	OPT B	RATE (mg/kg-hr) NORM	RATE (mg/kg-hr) OPT A	RATE (mg/kg-hr) OPT B	PERIOD RELEASE (mg/kg) NORM	PERIOD RELEASE (mg/kg) OPT A	PERIOD RELEASE (mg/kg) OPT B	TOTAL RELEASE (mg/kg) NORM	TOTAL RELEASE (mg/kg) OPT A	TOTAL RELEASE (mg/kg) OPT B
1	3	2	149	191	170	149	160	155	149	250	200	0	0	0	0	0	0	0	0	0
3	4	1	191	274	233	160	180	170	250	300	275	0	0	0	0	0	0	0	0	0
4	5	1	274	302	288	180	200	190	300	350	325	0	0	0	0	0	0	0	0	0
5	6	1	302	357	330	200	220	210	350	425	388	0	0	0	0	0	0	0	0	0
6	7	1	357	399	378	220	270	245	425	550	488	0	0	0	0	0	0	0	0	0
7	8	1	399	454	427	270	320	295	550	630	590	0	0	0	0	0	0	0	0	0
8	9	1	454	496	475	320	370	345	630	680	655	0	0	0	0	0	0	0	0	0
9	10	1	496	524	510	370	420	395	680	720	700	0	0	0	0	0	0	0	0	0
10	11	1	524	621	573	420	470	445	720	820	770	0	0	1	0	0	1	0	0	1
11	12	1	621	718	670	470	520	495	820	920	870	0	0	3	0	0	3	0	0	4
12	13	1	718	774	746	520	620	570	920	1024	972	0	0	19	0	0	19	0	0	24
13	15	2	774	857	816	620	720	670	1024	1038	1031	1	0	40	3	0	97	3	0	120
15	16	1	857	954	906	720	820	770	1038	1010	1024	6	1	43	6	1	43	9	1	140
16	16	0	954	996	975	820	820	820	1010	954	982	20	1	23	0	0	10	9	1	140
16	17	1	996	1024	1010	820	920	870	954	899	927	35	3	9	35	3	9	44	4	140
17	18	1	1024	1038	1031	920	1038	979	899	732	816	48	22	1	48	22	1	93	26	140
18	19	1	1038	1010	1024	1038	1010	1024	732	691	712	43	43	0	43	43		136	69	140
19	21	2	1010	954	982	1010	954	982	691	593	642	23	23	0	45	45		140	115	140
21	22	1	954	899	927	954	899	927	593	510	552	9	9	0	9	9		140	124	140
22	23	1	899	732	816	899	732	816	510	427	469	1	1	0	1	1		140	125	140
23	23	0	732	691	712	732	691	712	427	260	344	0	0	0				140	125	140
23	24	1	691	593	642	691	593	642	260	260	260	0	0	0				140	125	140
24	25	1	593	510	552	593	510	552	260	260	260	0	0	0				140	125	140
25	27	2	510	427	469	510	427	469				0	0	0				140	125	140
27	28	1	427	260	344	427	260	344				0	0	0				140	125	140
28	29	1	260	260	260	260	260	260				0	0	0				140	125	140

TABLE 6

POLLUTECH

EFFECT OF KILN CHANGE ON RATE
SAMPLE 105 AT GIVEN FLUORIDE RATE

TIME START	END	ELAPSE	LOW	HIGH	NORM	MID TEMPERATURE (C) LOW	HIGH	OPT A	LOW	HIGH	OPT B	RATE (mg/kg-hr) NORM	OPT A	OPT B	PERIOD RELEASE (mg/kg) NORM	OPT A	OPT B	TOTAL RELEASE (mg/kg) NORM	OPT A	OPT B
0	4	4	177	510	344	177	220	199	177	350	264	0	0	0	0	0	0	0	0	0
4	9	5	510	677	594	220	320	270	350	580	465	0	0	0	2	0	0	2	0	0
9	15	6	677	774	726	320	400	360	580	750	665	2	0	1	13	0	7	16	0	7
15	20	5	774	885	830	400	720	560	750	941	846	7	0	0	34	1	40	49	1	46
20	24	4	885	941	913	720	1024	872	941	1024	983	15	10	27	60	41	110	109	42	156
24	28	4	941	1024	983	1024	1038	1031	1024	1038	1031	27	41	41	110	164	164	219	206	200
28	30	2	1024	1038	1031	1038	635	837	1038	635	837	41	7	7	82	15	15	200	221	200
30	36	6	1038	635	837	635	621	628	635	621	628	7	1	1	44	4	4	200	225	200
36	44	8	635	621	628	621	454	538	621	454	538	1	0	0	5	1	1	200	226	200
44	50	6	621	454	538	454	454	454	454			0	0	0	1	0	0	290	227	200
50	55	5	454	454	454							0	0	0	0	0	0	200	227	200

TABLE 7

POLLUTECH

EFFECT OF KILN CHANGE ON RATE
SAMPLE 107 AT GIVEN FLUORIDE RATE

TIME START	TIME END	ELAPSE	LOW	HIGH	NORM	MID TEMPERATURE (C) LOW	HIGH	OPT A	LOW	HIGH	OPT B	RATE (mg/kg-hr) NORM	OPT A	OPT B	PERIOD RELEASE (mg/kg) NORM	OPT A	OPT B	TOTAL RELEASE (mg/kg) NORM	OPT A	OPT B
11	13	2	371	427	399	371	390	381	371	400	426	0	0	0	0	0	0	0	0	0
13	15	2	427	482	455	390	420	405	400	600	540	0	0	0	0	0	0	0	0	0
15	17	2	482	524	503	420	430	425	600	746	673	0	0	0	0	0	0	0	0	0
17	20	3	524	649	587	430	450	440	746	871	809	0	0	3	0	0	10	0	0	10
20	22	2	649	746	698	450	550	500	871	916	894	0	0	21	0	0	43	0	0	53
22	24	2	746	871	809	550	650	600	916	943	930	3	0	44	7	0	89	7	0	142
24	26	2	871	916	894	650	750	700	943	977	960	21	0	81	43	0	162	50	0	304
26	28	2	916	943	930	750	850	800	977	982	980	44	3	117	89	5	235	139	6	538
28	30	2	943	977	960	850	977	914	982	982	982	81	32	123	162	64	246	300	70	570
30	32	2	977	982	980	977	982	980	982	977	980	117	117	117	235	235	235	535	305	570
32	34	2	982	982	982	982	982	982	977	910	944	123	123	59	246	246	117	570	551	570
34	36	2	982	977	980	982	977	980	910	843	877	117	117	15	235	235	30	570	570	570
36	38	2	977	910	944	977	910	944	843	621	732	59	59	1	117	117	1	570	570	570
38	40	2	910	843	877	910	843	877	621	552	587	15	15	0	30	30		570	570	570
40	42	2	843	621	732	843	621	732	552	427	490	1	1	0	1	1		570	570	570
42	44	2	621	552	587	621	552	587			0	0	0	0				570	570	570
44	45	1	552	427	490	552	427	490			0	0	0	0				570	570	570

TABLE 8

EFFECT OF KILN CHANGE ON RATE
SAMPLE 100 AT GIVEN FLUORIDE RATE

TIME						MID TEMPERATURE (C)						RATE (mg/kg-hr)			PERIOD RELEASE (mg/kg)			TOTAL RELEASE (mg/kg)		
START	END	ELAPSE	LOW	HIGH	NORM	LOW	HIGH	OPT A	LOW	HIGH	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B
0	4	4	204	538	371	204	250	227	204	400	342	0	0	0	0	0	0	0	0	0
4	6	2	538	593	566	250	350	300	400	720	600	0	0	0	0	0	0	0	0	0
6	9	3	593	871	732	350	620	485	720	927	824	1	0	5	4	0	14	4	0	15
9	11	2	871	927	899	620	820	720	927	1038	983	14	1	40	20	2	80	31	2	95
11	13	2	927	1038	983	820	1038	929	1038	1043	1041	40	20	80	80	41	159	111	43	254
13	17	4	1038	1043	1041	1038	1043	1041	1043	593	818	80	80	4	319	319	18	390	362	272
17	21	4	1043	593	818	1043	593	818	593	538	566	4	4	0	18	18	0	390	380	272
21	23	2	593	538	566	593	538	566	538	149	344	0	0	0	0	0	0	390	380	272
23	26	3	538	149	344	538	149	344				0	0	0	0	0		390	380	272

TABLE 9

POLLUTECH

```
EFFECT OF KILN CHANGE ON RATE
SAMPLE 109 AT GIVEN FLUORIDE RATE      RUN 1

          TIME                                        MID TEMPERATURE (C)                                   RATE (mg/kg-hr)        PERIOD RELEASE (mg/kg)    TOTAL RELEASE (mg/kg)
 START    END    ELAPSE    LOW    HIGH   NORM    LOW    HIGH   OPT A    LOW    HIGH   OPT B    NORM   OPT A   OPT B    NORM   OPT A   OPT B    NORM   OPT A   OPT B
 -----------------------  ------------------------------------------------------------------  ---------------------  ---------------------  ---------------------

     0      4       4      204     538    371    204     250    227     204     500    352       0       0       0       0       0       0       0       0       0
     4      6       2      538     593    566    250     350    300     500     650    575       0       0       0       0       0       0       0       0       0
     6      9       3      593     871    732    350     620    485     650     927    789       0       0       1       1       0       3       1       0       3
     9     11       2      871     927    899    620     820    720     927    1038    983       7       0      27      15       1      53      16       1      57
    11     13       2      927    1038    983    820    1038    929    1038    1049   1044      27      12      63      53      24     126      70      25     183
    13     17       4     1038    1049   1044   1038    1049   1044    1049     593    821      63      63       2     253     253       8     322     277     191
    17     21       4     1049     593    821   1049     593    821     593     538    566       2       2       0       8       8       0     331     286     191
    21     23       2      593     538    566    593     538    566     538     149    344       0       0       0       0       0       0     331     286     191
    23     26       3      538     149    344    538     149    344                               0       0       0       0       0              331     286     191


EFFECT OF KILN CHANGE ON RATE
SAMPLE 109 AT GIVEN FLUORIDE RATE      RUN 2

          TIME                                        MID TEMPERATURE (C)                                   RATE (mg/kg-hr)        PERIOD RELEASE (mg/kg)    TOTAL RELEASE (mg/kg)
 START    END    ELAPSE    LOW    HIGH   NORM    LOW    HIGH   OPT A    LOW    HIGH   OPT B    NORM   OPT A   OPT B    NORM   OPT A   OPT B    NORM   OPT A   OPT B
 -----------------------  ------------------------------------------------------------------  ---------------------  ---------------------  ---------------------

     0      4       4      204     538    371    204     250    227     204     500    352       0       0       0       0       0       0       0       0       0
     4      6       2      538     593    566    250     350    300     500     650    575       0       0       0       0       0       0       0       0       0
     6      9       3      593     871    732    350     620    485     650     927    789       3       0       7       9       0      20       9       6      21
     9     11       2      871     927    899    620     820    720     927    1038    983      30       2      83      60       5     166      70       5     186
    11     13       2      927    1038    983    820    1038    929    1038    1049   1044      83      44     164     166      88     328     235      93     514
    13     17       4     1038    1049   1044   1038    1049   1044    1049     593    821     164     164      11     656     656      43     610     610     557
    17     21       4     1049     593    821   1049     593    821     593     538    566      11      11       0      43      43       1     610     610     558
    21     23       2      593     538    566    593     538    566     538     149    344       0       0       0       0       0       0     610     610     558
    23     26       3      538     149    344    538     149    344                               0       0       0       0       0              610     610     558
```

TABLE 10

EFFECT OF KILN CHANGE ON RATE
SAMPLE 110 AT GIVEN FLUORIDE RATE

	TIME					MID TEMPERATURE (C)						RATE (mg/kg-hr)			PERIOD RELEASE (mg/kg)			TOTAL RELEASE (mg/kg		
START	END	ELAPSE	LOW	HIGH	NORM	LOW	HIGH	OPT A	LOW	HIGH	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B	NORM	OPT A	OPT B
0	3	3	399	543	471	399	400	400	399	550	475	0	0	0	0	0	0	0	0	0
3	6	3	543	560	552	400	400	400	550	675	613	0	0	0	0	0	1	0	0	1
6	10	4	560	749	655	400	420	410	675	950	813	1	0	9	3	0	34	4	0	36
10	13	3	749	816	783	420	450	435	950	1010	980	6	0	64	17	0	192	21	0	228
13	17	4	816	943	880	450	650	550	1010	1079	1045	28	0	127	80	1	508	101	1	540
17	20	3	943	1010	977	650	880	765	1079	1077	1078	62	4	178	185	13	534	286	14	540
20	22	2	1010	1079	1045	880	1079	980	1077	1077	1077	127	64	176	254	127	353	540	141	540
22	24	2	1079	1077	1078	1079	1077	1078	1077	1077	1077	178	178	176	356	356	353	540	498	540
24	26	2	1077	1077	1077	1077	1077	1077	1077	1077	1077	176	176	176	353	353	353	540	540	540
26	29	3	1077	1077	1077	1077	1077	1077	1077	732	905	176	176	27	529	529	81	540	540	540
29	31	2	1077	1077	1077	1077	1077	1077	732	566	649	176	176	1	353	353	2	540	540	540
31	33	2	1077	1077	1077	1077	1077	1077	566	482	524	176	176	0	353	353	0	540	540	540
33	36	3	1077	732	905	1077	732	905	482	385	434	27	27	0	81	81	0	540	540	540
36	37	1	732	566	649	732	566	649	385	304	345	1	1	0	1	1		540	540	540
37	40	3	566	482	524	566	482	524				0	0	0	0	0		540	540	540
40	44	4	482	385	434	482	385	434				0	0	0				540	540	540
44	46	2	385	304	345	385	304	345				0	0	0				540	540	540

TABLE 11

POLLUTECH

EFFECT OF KILN CHANGE ON RATE
SAMPLE 111 AT GIVEN FLUORIDE RATE

TIME START	END	ELAPSE	LOW	HIGH	NORM	MID TEMPERATURE (C) LOW	HIGH	OPT A	LOW	HIGH	OPT B	RATE (mg/kg-hr) NORM	OPT A	OPT B	PERIOD RELEASE (mg/kg) NORM	OPT A	OPT B	TOTAL RELEASE (mg/kg) NORM	OPT A	OPT B
4	10	6	260	704	482	260	300	280	260	300	280	0	0	0	0	0	0	0	0	0
10	16	6	704	788	746	300	350	325	300	450	375	1	0	0	7	0	0	7	0	0
16	24	8	788	899	844	350	850	600	450	900	675	0	0	0	62	0	2	69	0	2
24	26	2	899	920	910	850	900	875	900	1024	962	25	14	58	49	27	117	119	28	119
26	30	4	920	1024	972	900	1024	962	1024	1049	1037	68	58	183	274	233	733	392	261	459
30	32	2	1024	1049	1037	1024	1049	1037	1049	800	925	183	183	32	366	366	63	459	459	459
32	36	4	1049	910	980	1049	800	925	800	663	732	77	32	1	308	127	3	459	459	459
36	42	6	910	663	787	800	663	732	663	663	663	3	1	0	16	5	1	459	459	459
42	47	5	663	663	663	663	663	663				0	0	0	1	1		459	459	459

TABLE 12

POLLUTECH

FLUORIDE RELEASE FROM TEMPERATURE MODEL

SAMPLE CODE	RAW F1 (mg/kg)	FLUORIDE RELEASE (mg/kg) UP TO FIRING NORMAL	OPTION A	OPTION B	TOTAL PERIOD NORMAL	OPTION A	OPTION B	FLUORIDE RELEASE (%) UP TO FIRING NORMAL	OPTION A	OPTION B	TOTAL PERIOD NORMAL	OPTION A	OPTION B
100	620	452	325	314	620	540	526	73	52	51	100	87	85
102	286	286	257	267	286	286	286	100	90	93	100	100	100
103	620	620	575	620	620	620	620	100	93	100	100	100	100
104	140	93	26	140	140	125	140	66	19	100	100	89	100
105	280	280	206	200	280	227	280	100	74	71	100	81	100
107	570	535	305	538	570	570	570	94	54	94	100	100	100
108	390	390	362	254	390	380	272	100	93	65	100	97	70
109	610	610	610	514	610	610	558	100	100	84	100	100	91
110	540	540	498	540	540	540	540	100	92	100	100	100	100
111	459	459	459	459	459	459	459	100	100	100	100	100	100
AVERAGE	452	427	362	385	452	436	425	93	77	86	100	95	95

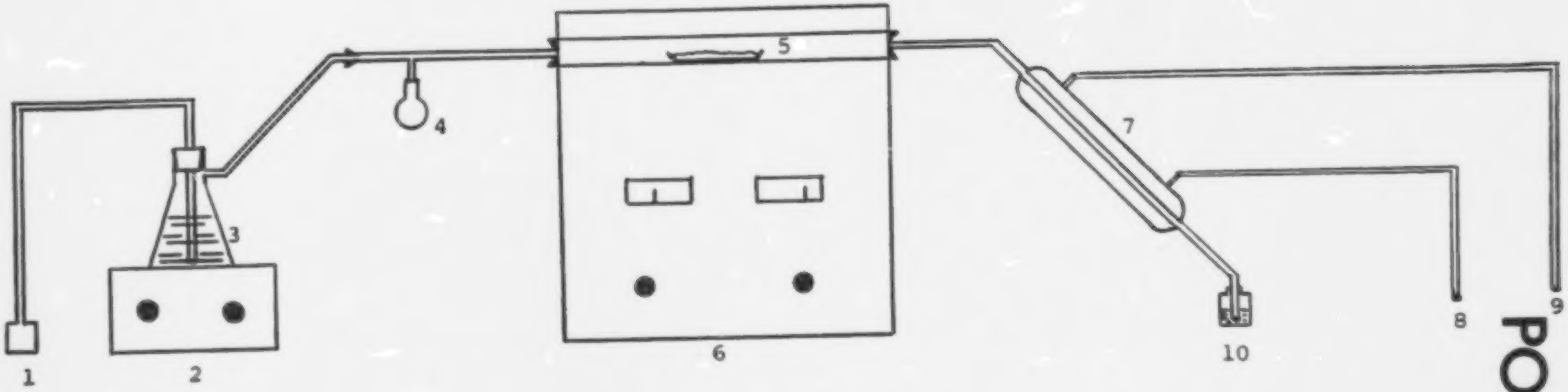
TABLE 13

POLLUTECH

FIGURES

FIGURE 1: PYROHYDROLYSIS UNIT

1. Air pump
2. Heater/stirrer unit
3. Fluoride free steam generator
4. Condensate trap
5. Sample boat
6. Tube furnace
7. Condensor
8. Cooling water input
9. To drain
10. Caustic sample trap



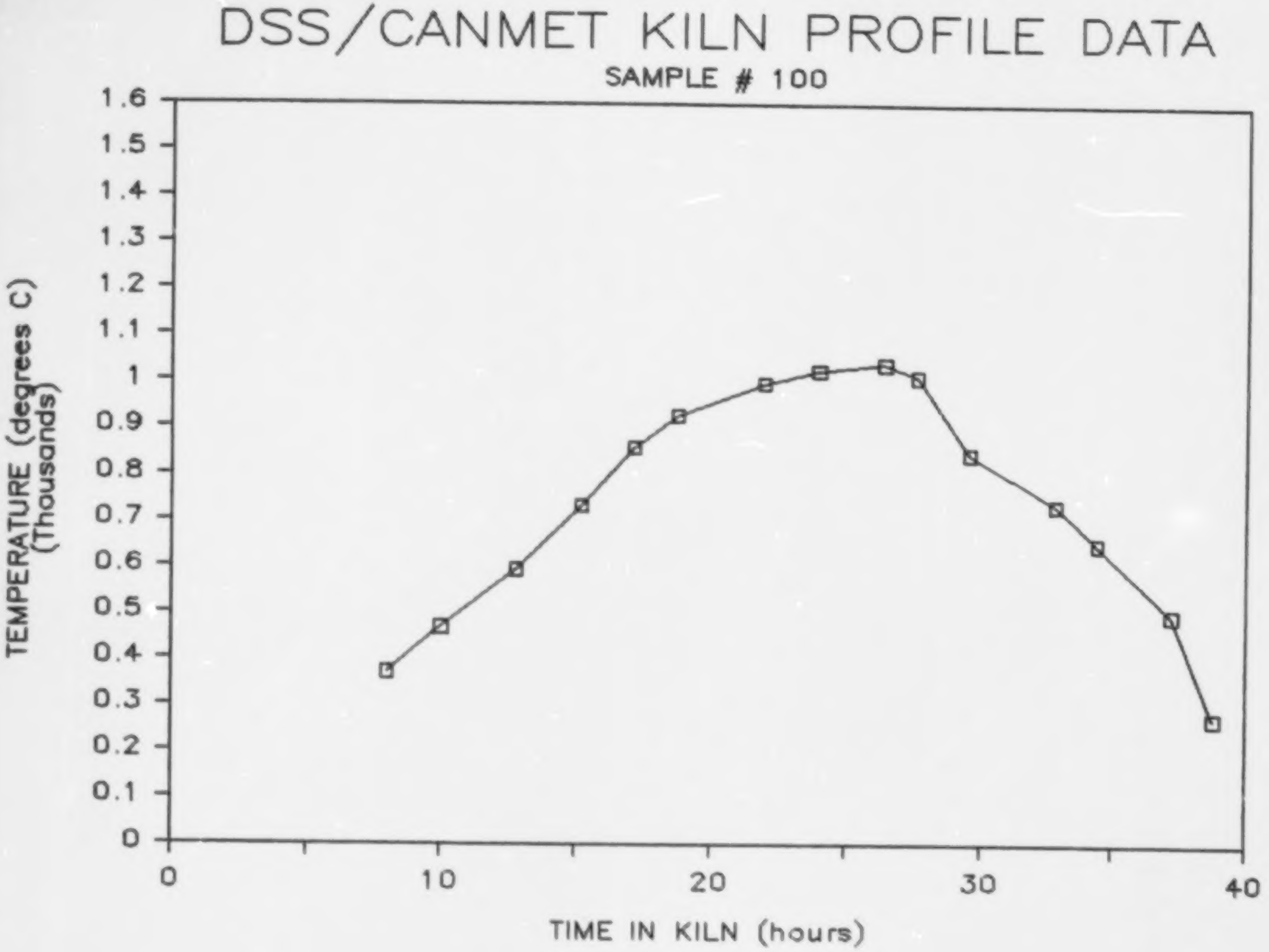


FIGURE 2

POLLUTECH

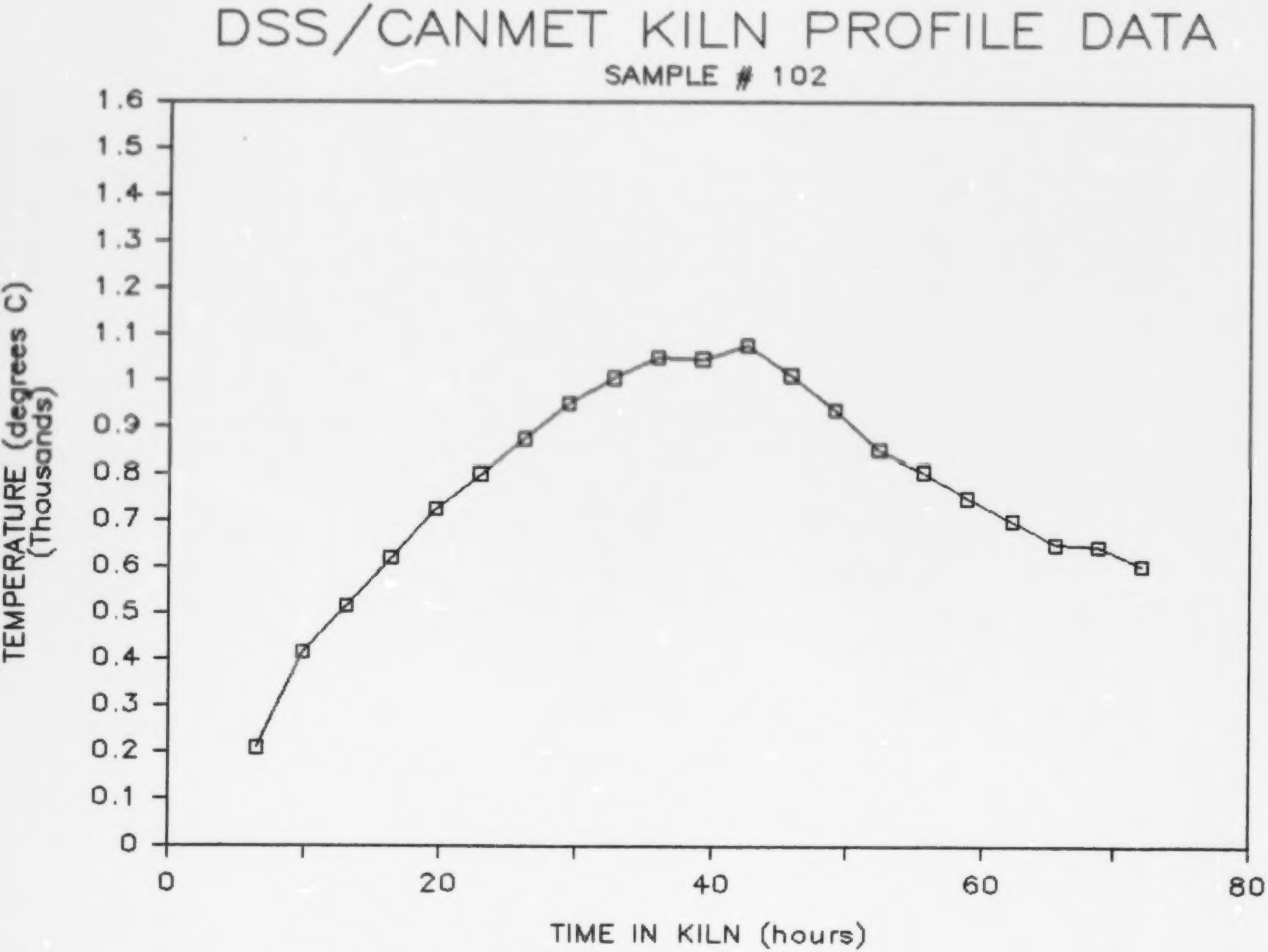

DSS/CANMET KILN PROFILE DATA
SAMPLE # 102
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
TIME IN KILN (hours)

FIGURE 3

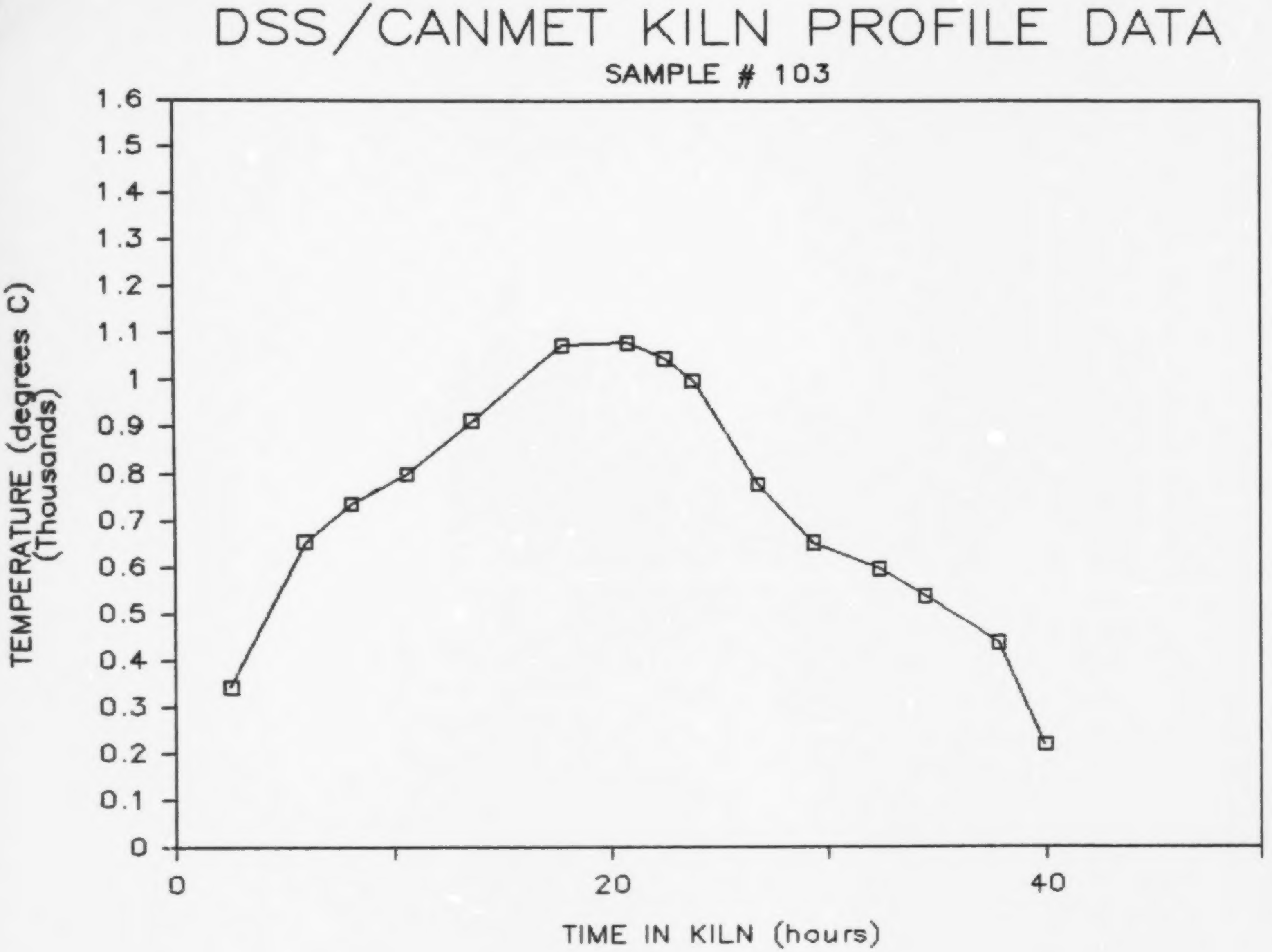

DSS/CANMET KILN PROFILE DATA
SAMPLE # 103
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 4

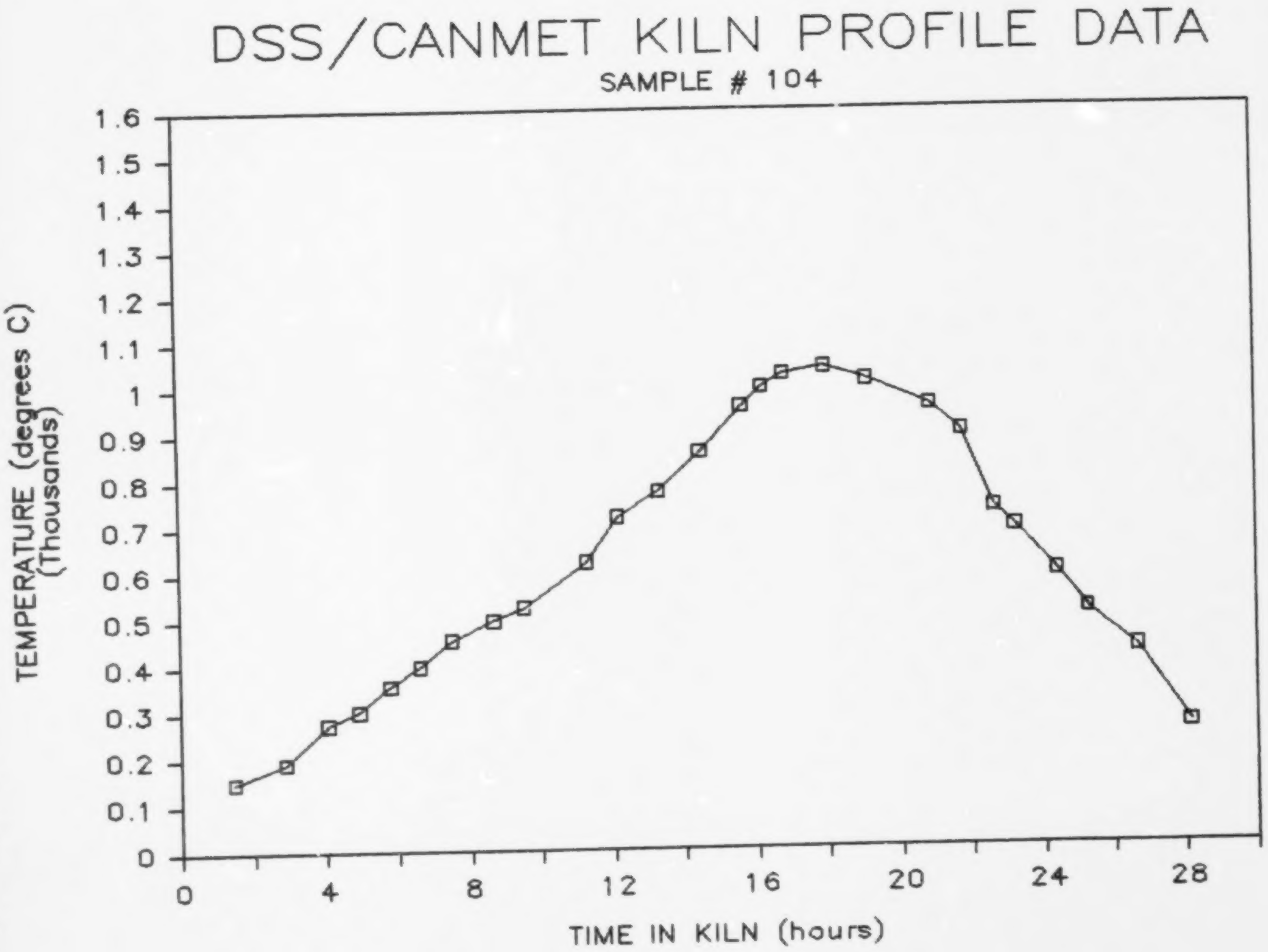
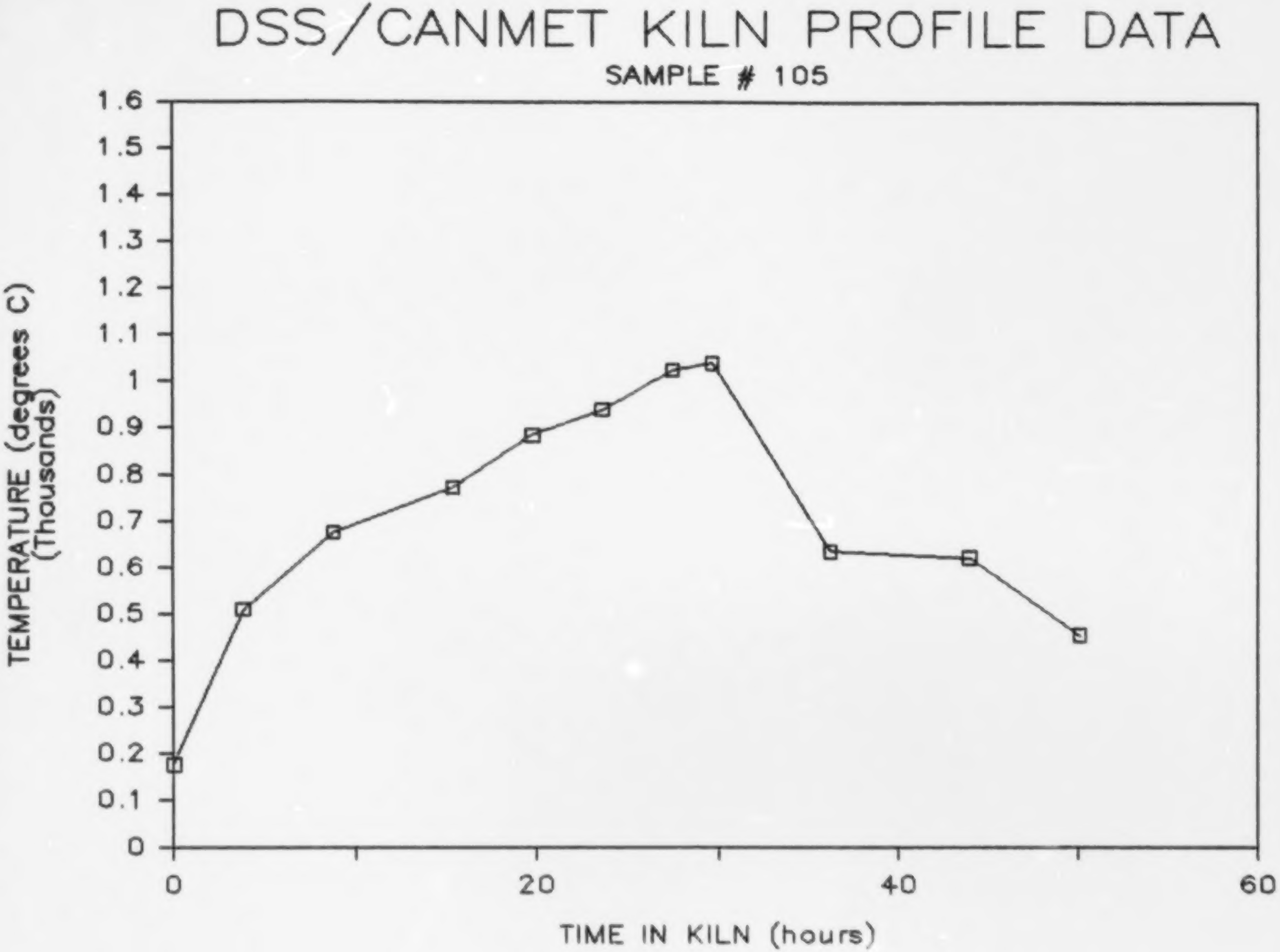


FIGURE 5

POLLUTECH



DSS/CANMET KILN PROFILE DATA

SAMPLE # 105

FIGURE 6

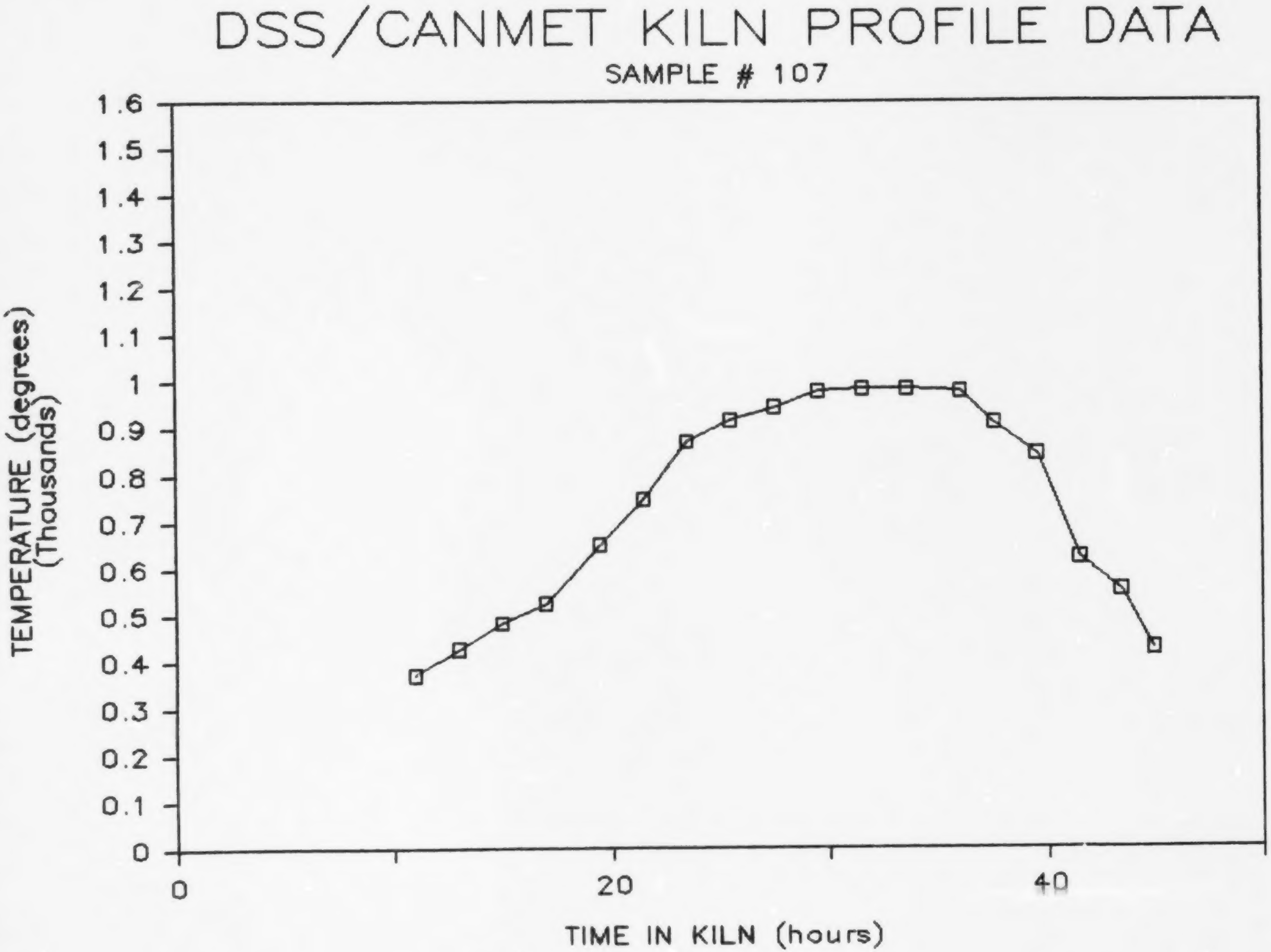

DSS/CANMET KILN PROFILE DATA
SAMPLE # 107
TEMPERATURE (degrees)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 7

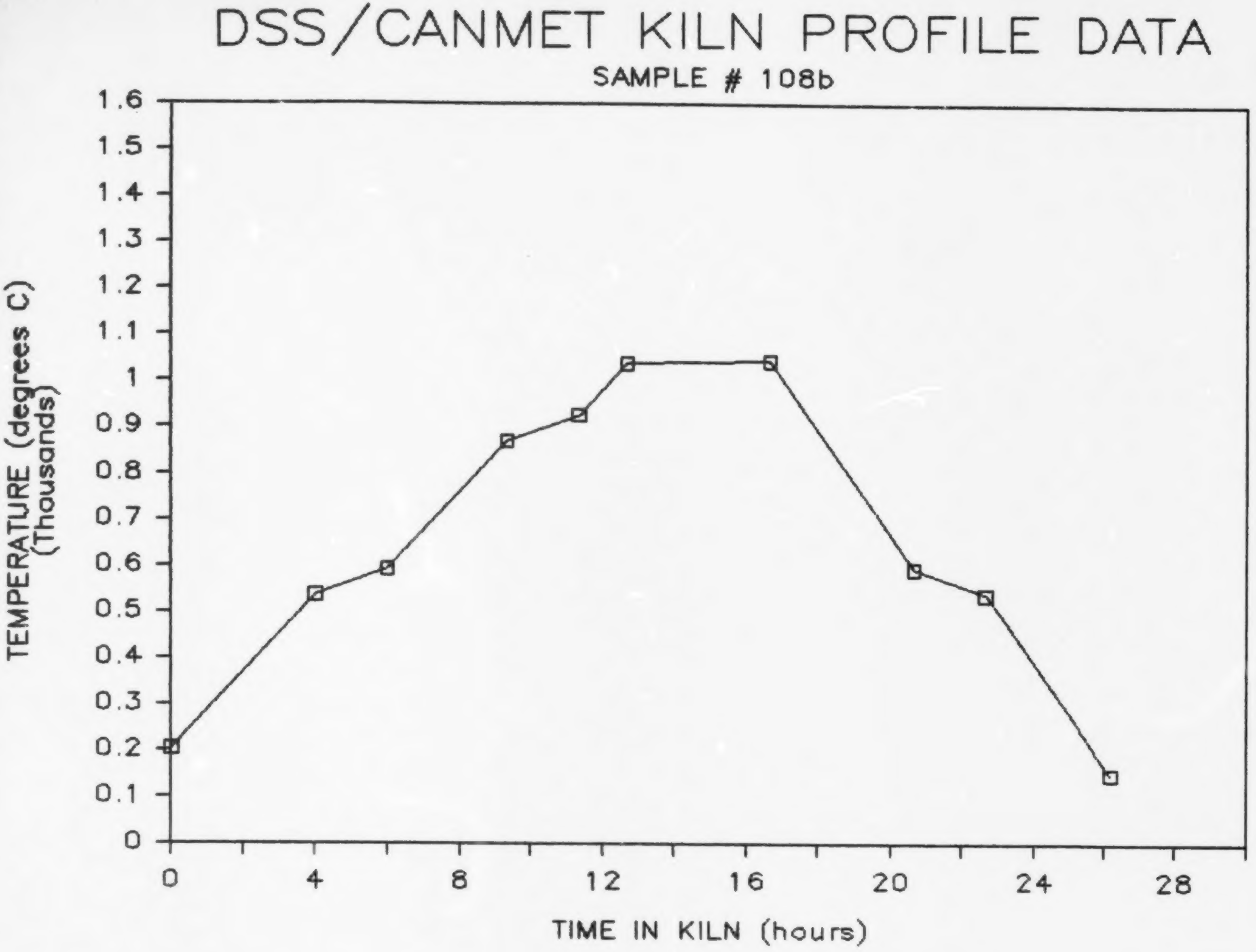
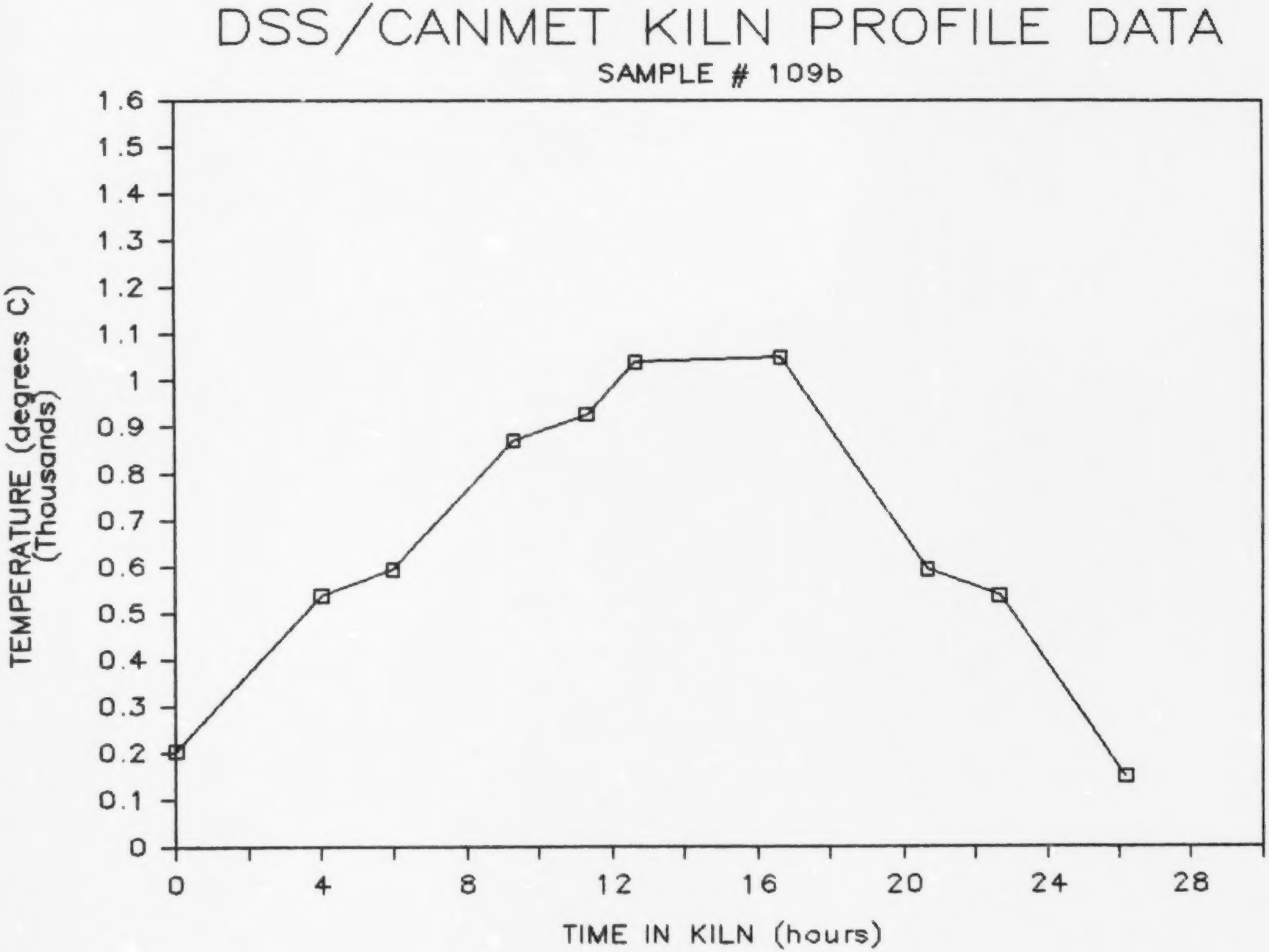

DSS/CANMET KILN PROFILE DATA
SAMPLE # 108b
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
4
8
12
16
20
24
28
TIME IN KILN (hours)

FIGURE 8



DSS/CANMET KILN PROFILE DATA

SAMPLE # 109b

FIGURE 9

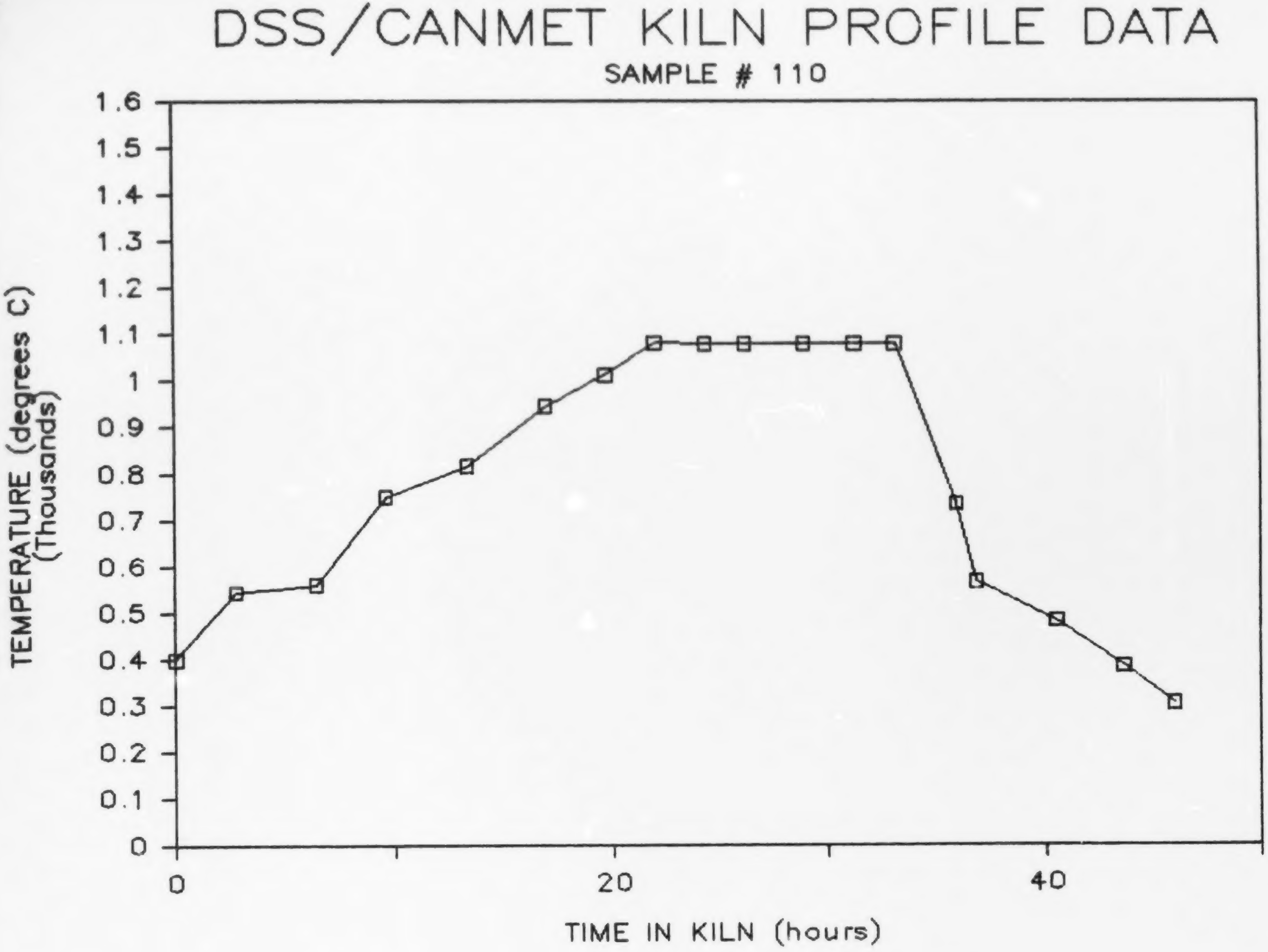

DSS/CANMET KILN PROFILE DATA
SAMPLE # 110
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 10

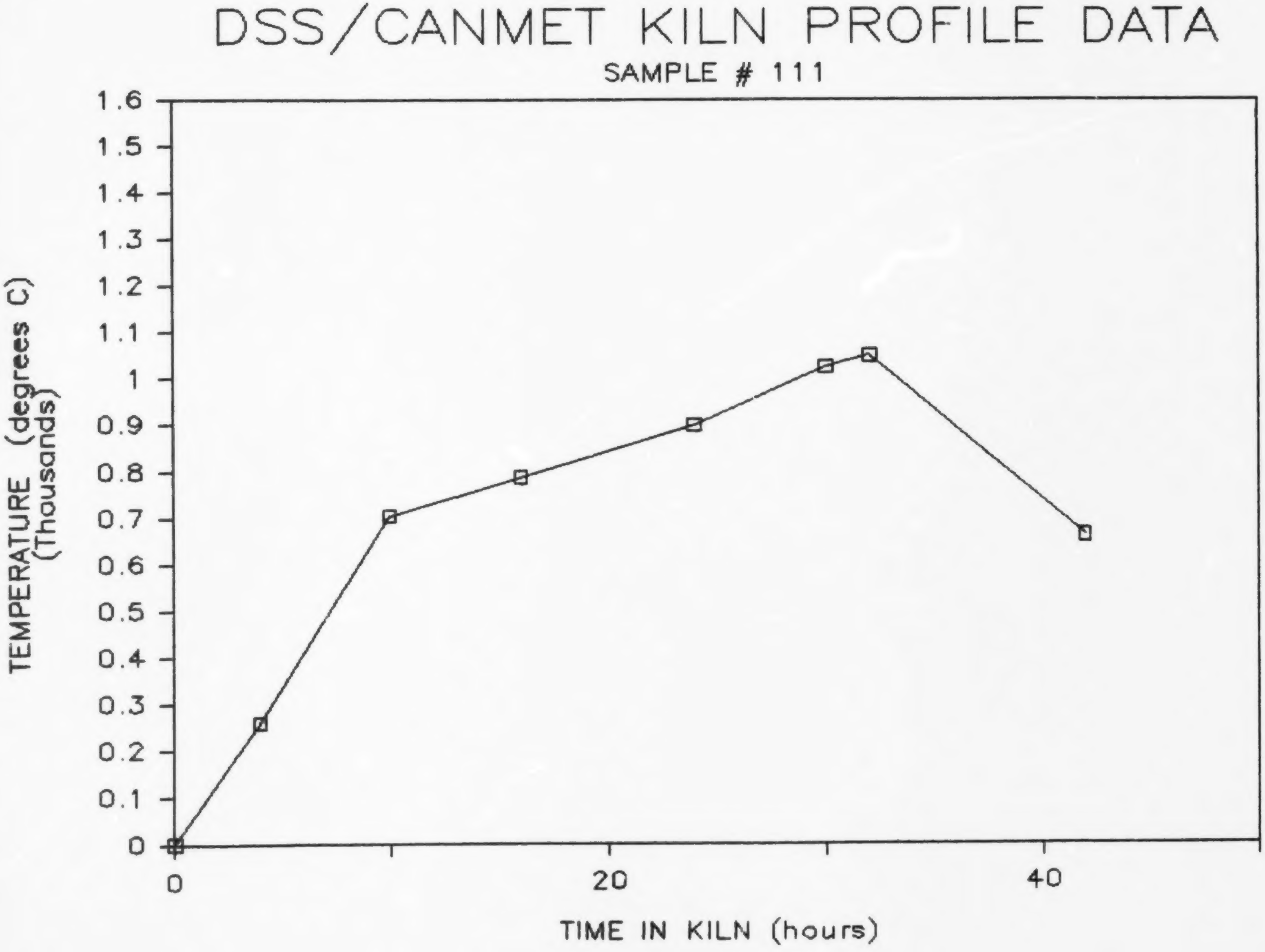
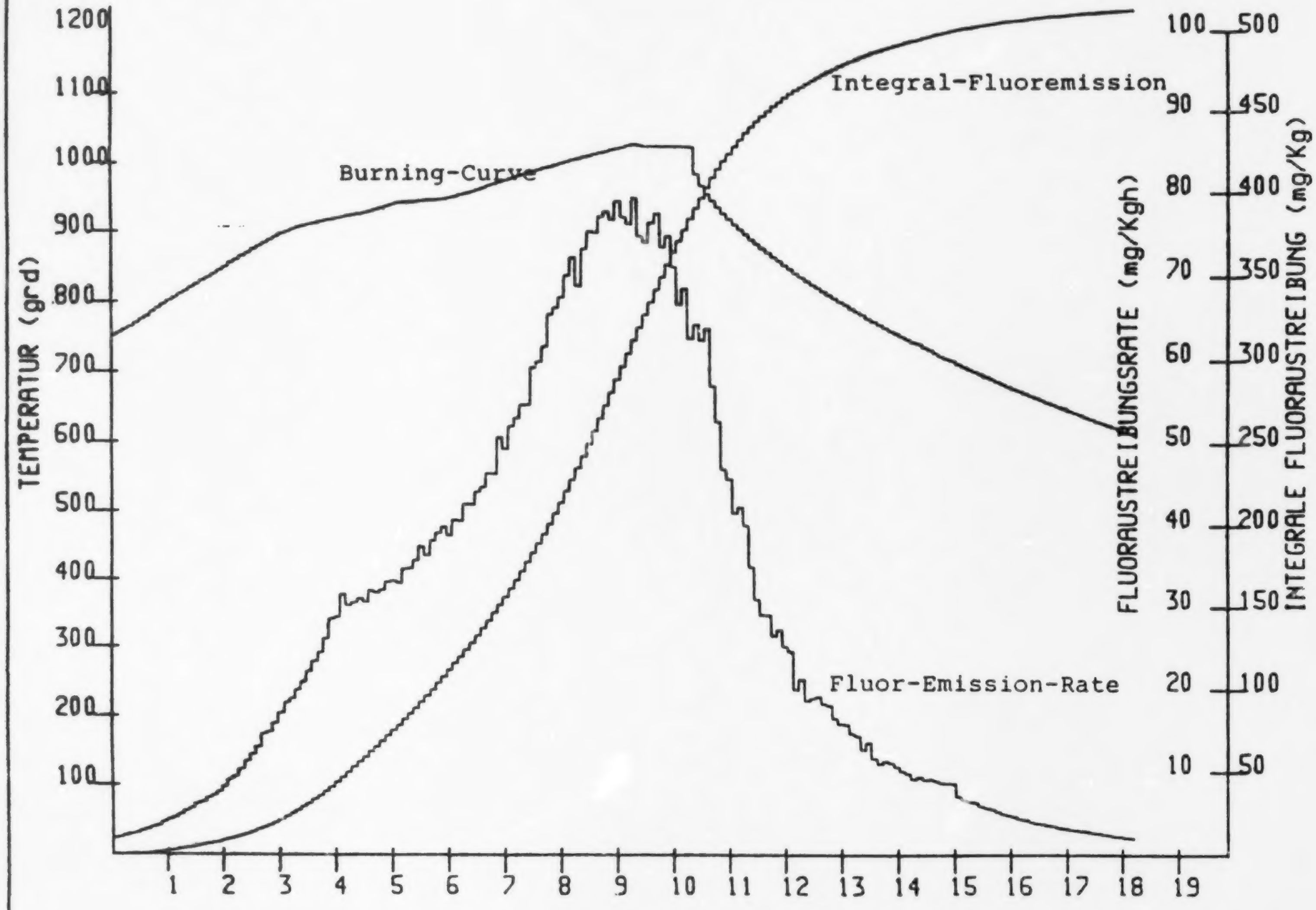

DSS/CANMET KILN PROFILE DATA
SAMPLE # 111
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 11

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 31 g/Kg TROCKENER LUFT

PROBE NR. 100



POLLUTECH

FIGURE 12

BRENNZEIT (h) Time of F-Emission

Dat.:29.11.1984
KT2706.2

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

PROBE NR.:102

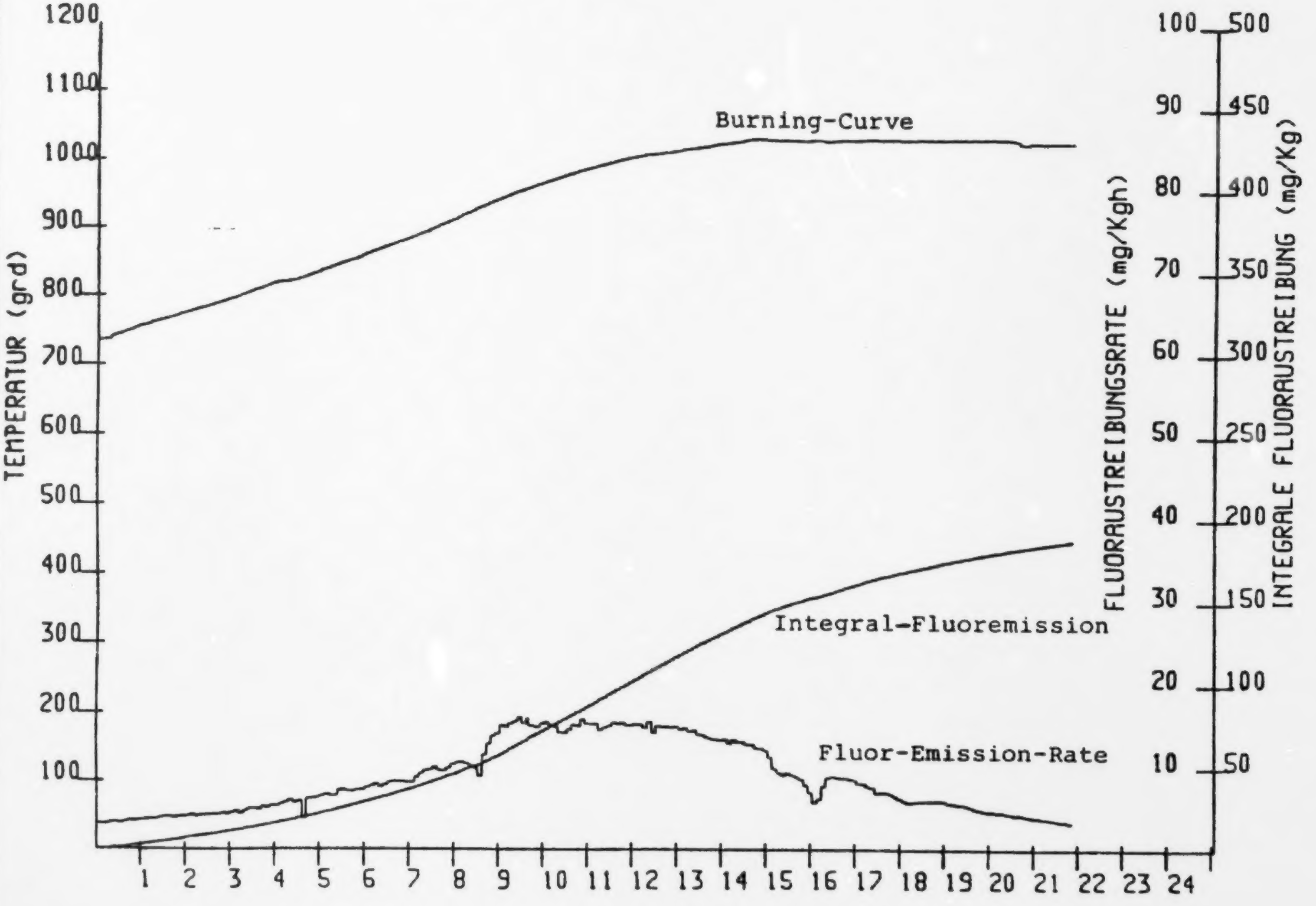


FIGURE 13

POLLUTECH

Dat.:10.12.1984
KT2706.5

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE NR.: 103

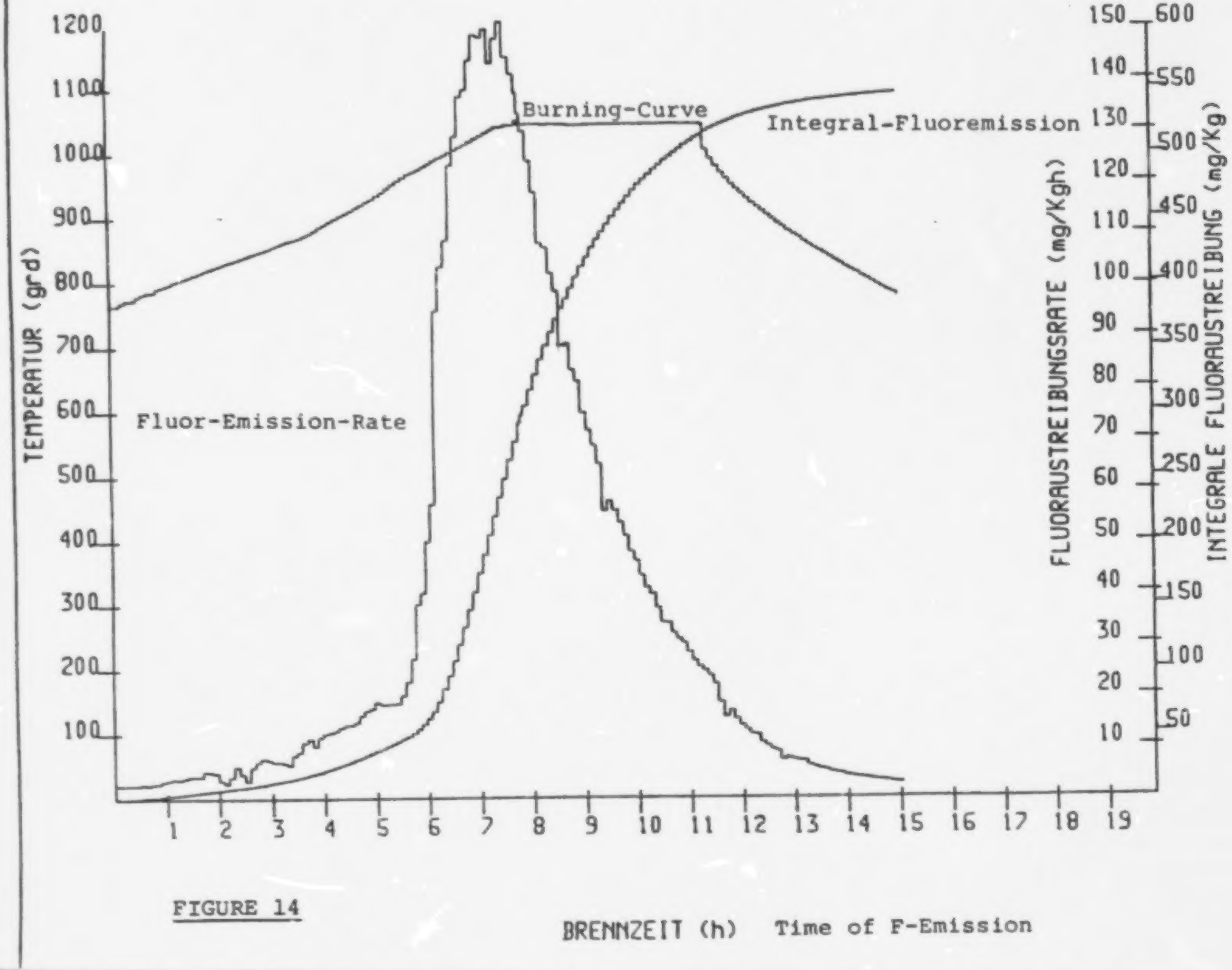


FIGURE 14

POLLUTECH

Dat.: 16.01.1985
KT27061.1

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 30 g/Kg TROCKENER LUFT

PROBE NR.: 104

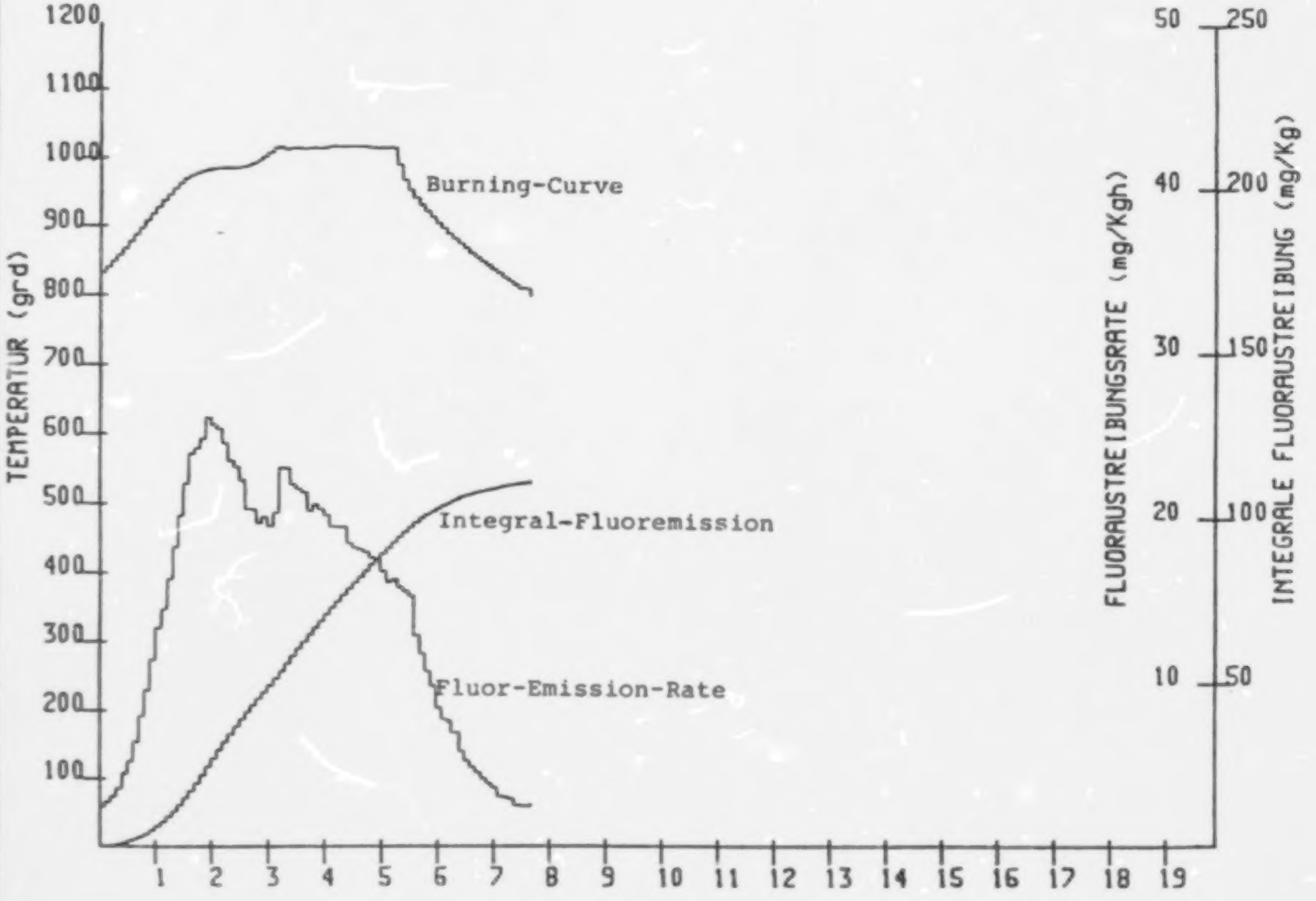


FIGURE 15

POLLUTECH

Dat.: 13.12.1984
KT2706.6

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

PROBE NR.: 105

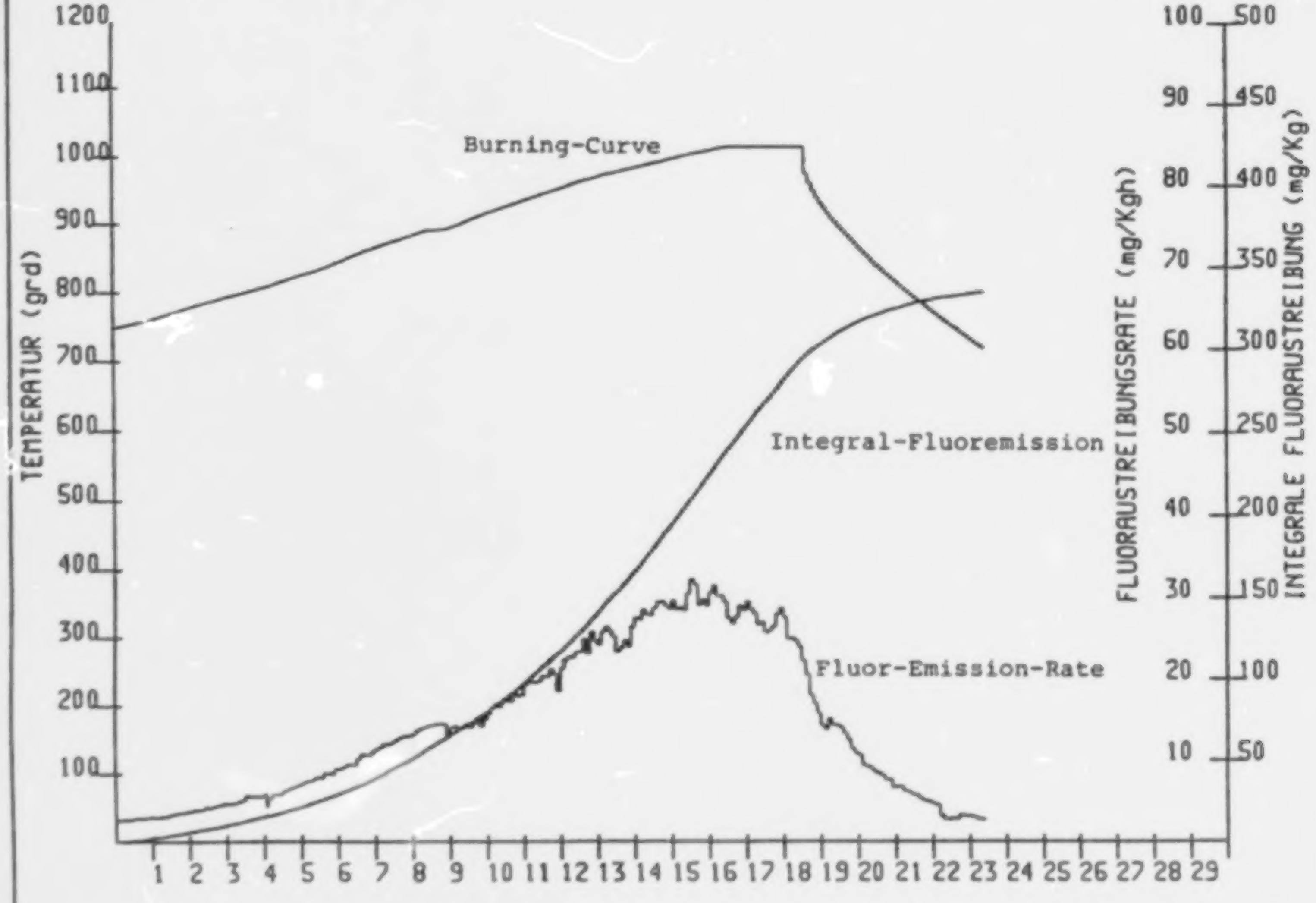


FIGURE 16

POLLUTECH

Dat.: 20.12.1985
KT2706.8

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE NR., 107

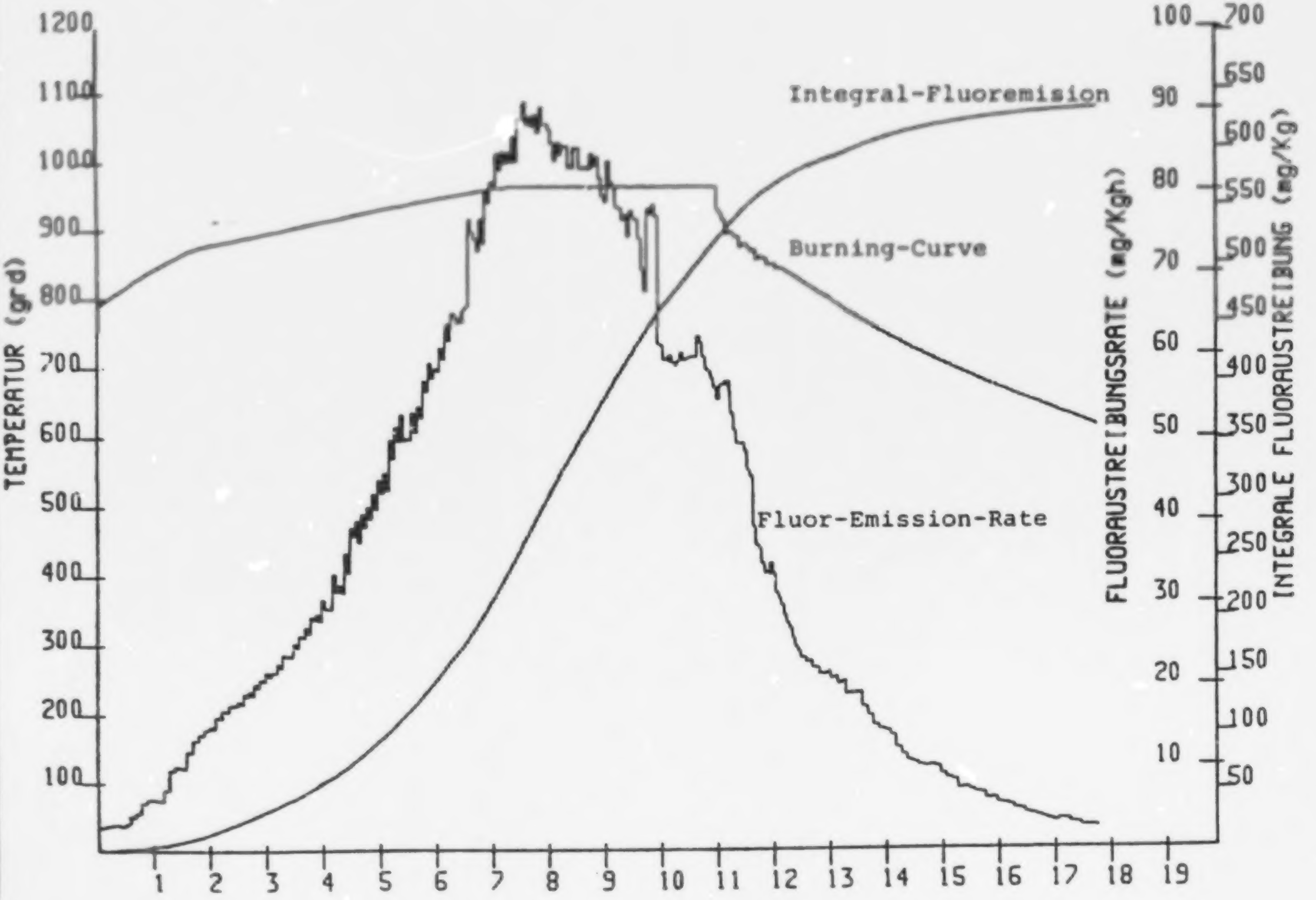


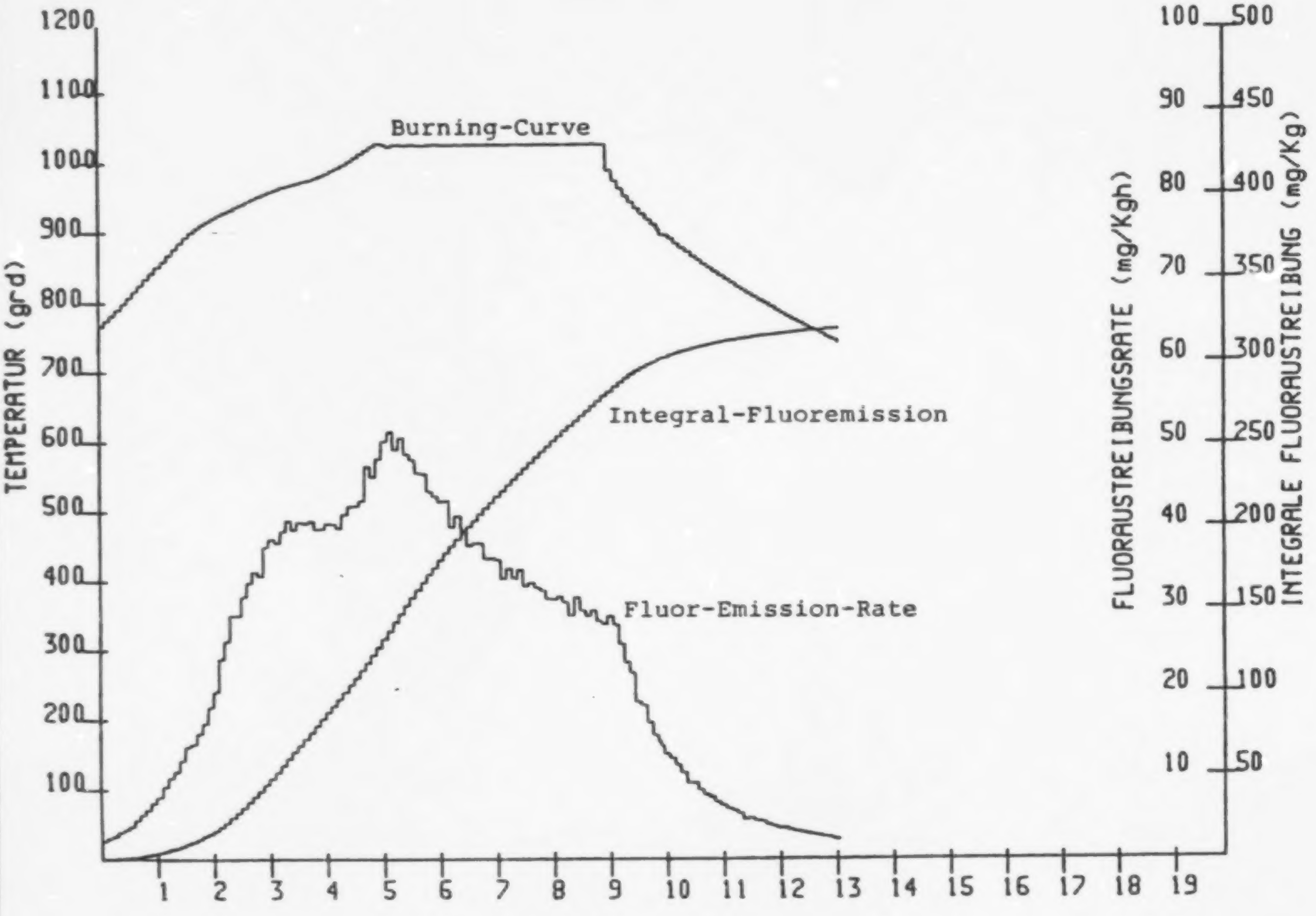
FIGURE 17

POLLUTECH

Dat.,23.01.1985
KT27061.3

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

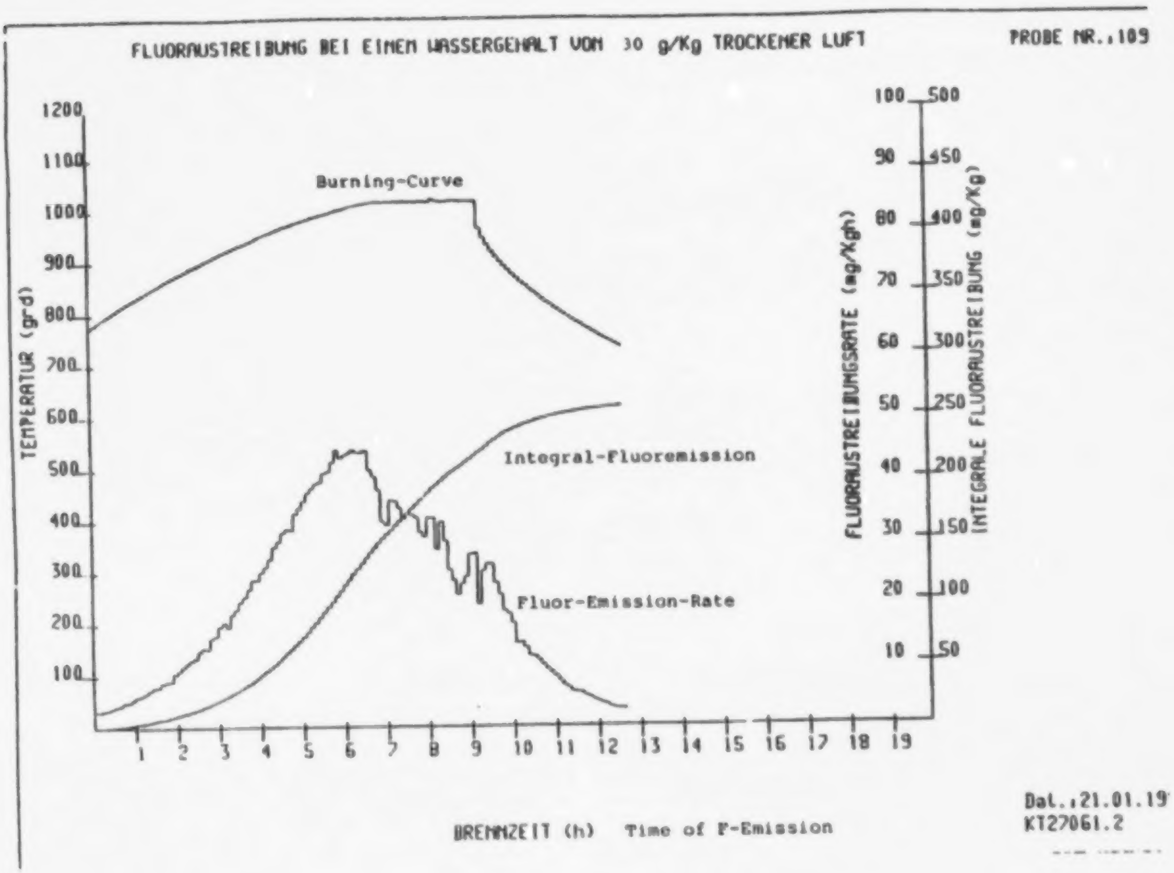
PROBE NR.: 108



POLLUTECH

FIGURE 18

Dat.: 03.12.1984
KT2706.3


FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 30 g/Kg TROCKENER LUFT
PROBE NR.: 109
TEMPERATUR (grd)
1200
1100
1000
900
800
700
600
500
400
300
200
100
Burning-Curve
Integral-Fluoremission
Fluor-Emission-Rate
FLUORAUSTREIBUNGSRATE (mg/Kgh)
INTEGRALE FLUORAUSTREIBUNG (mg/Kg)
100 500
90 450
80 400
70 350
60 300
50 250
40 200
30 150
20 100
10 50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
BRENNZEIT (h) Time of F-Emission
Dat.:21.01.19
KT27061.2

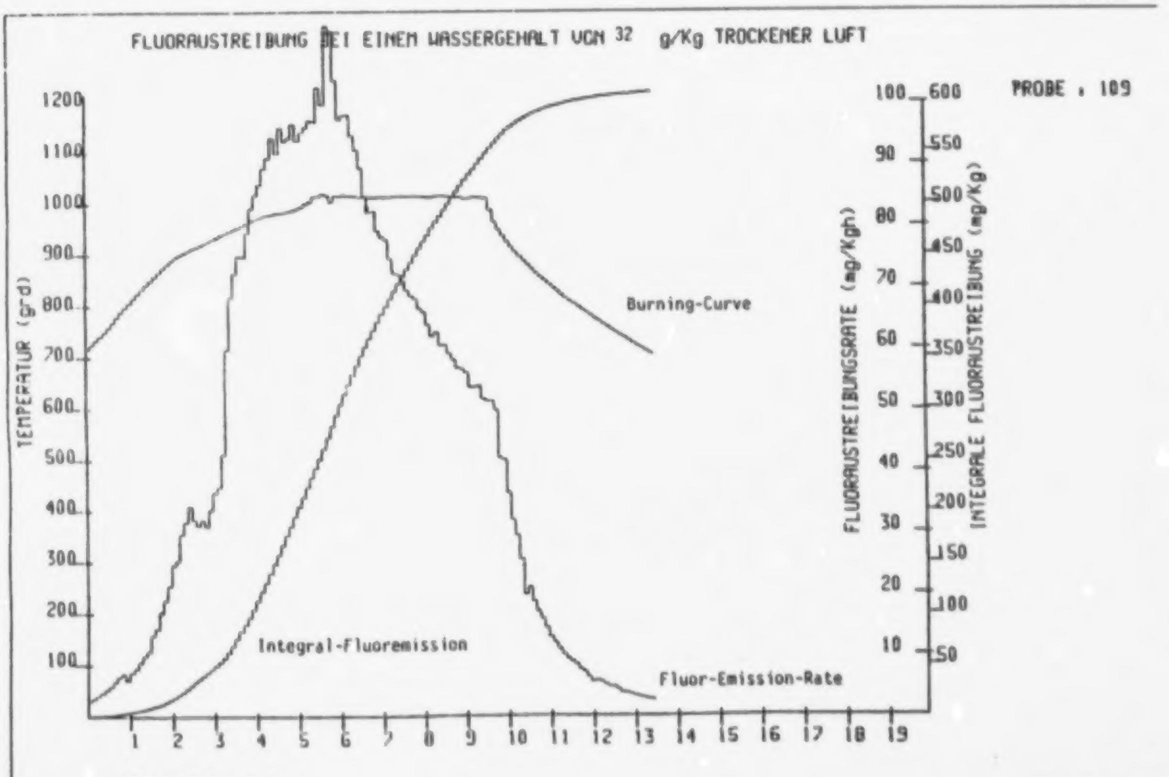

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT
PROBE : 109
TEMPERATUR (grd)
1200
1100
1000
900
800
700
600
500
400
300
200
100
Burning-Curve
Integral-Fluoremission
Fluor-Emission-Rate
FLUORAUSTREIBUNGSRATE (mg/Kgh)
INTEGRALE FLUORAUSTREIBUNG (mg/Kg)
100 600
90 550
80 500
450
70 400
60 350
50 300
40 250
30 200
150
20 100
10 50
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
Dat.:11.03.19
KT27061.5

FIGURE 19

BRENNZEIT (h) Time of F-Emission

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

PROB NR.:110

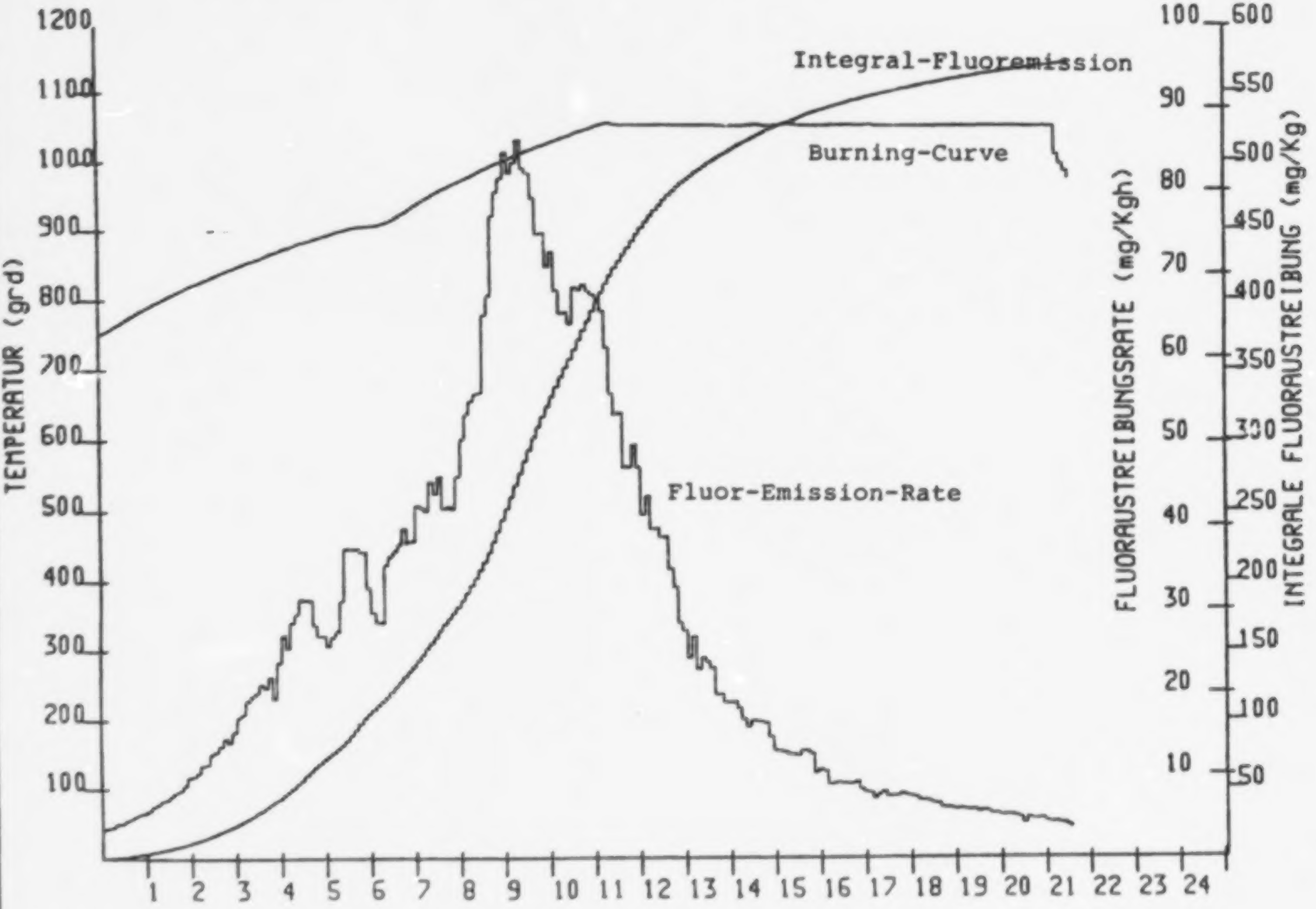


FIGURE 20

POLLUTECH

Dat.:10.01.1985
KT2706.9

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE :111

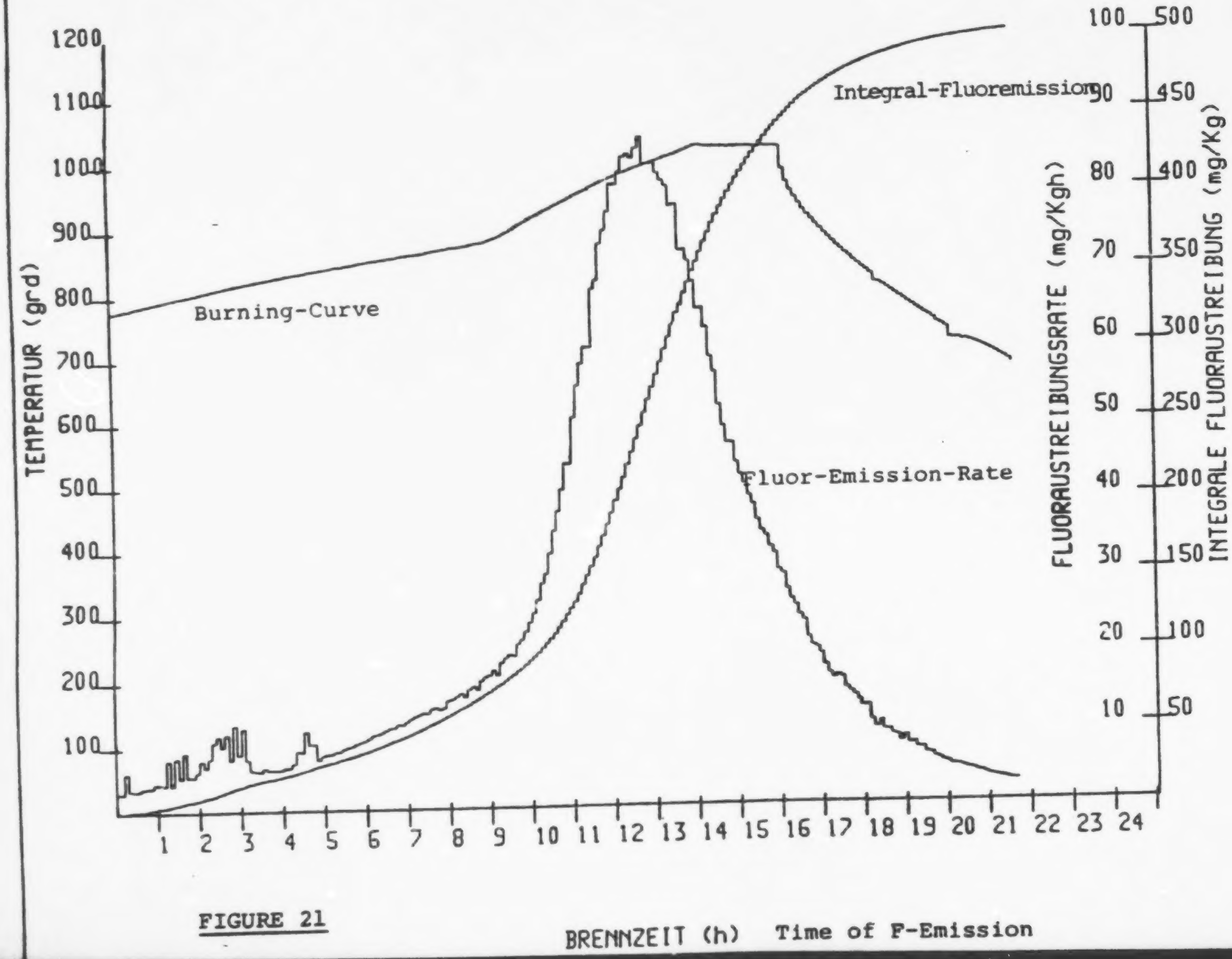


FIGURE 21

POLLUTECH

Dat.:25.02.1985
KT27061.4

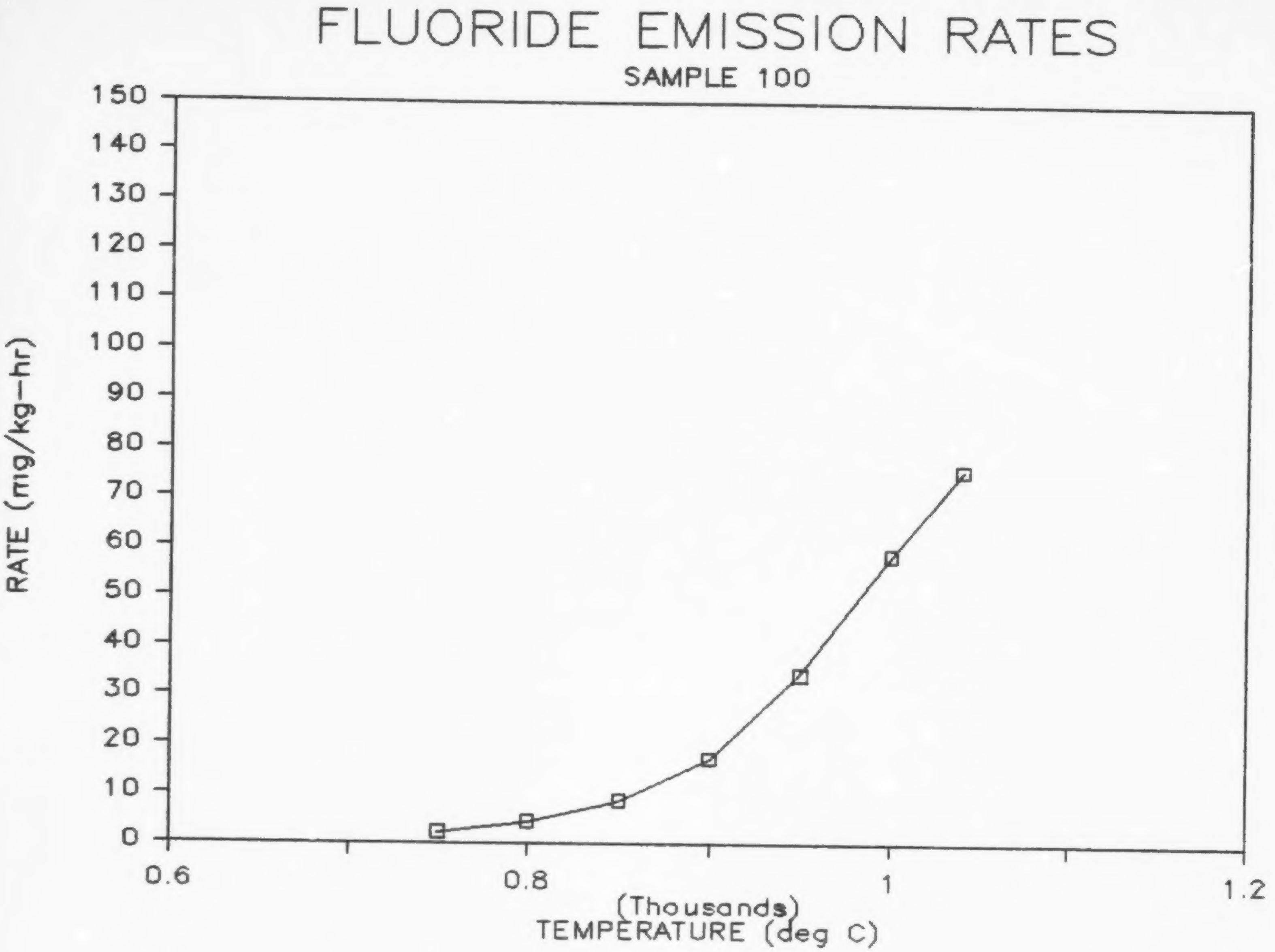

FLUORIDE EMISSION RATES
SAMPLE 100
RATE (mg/kg-hr)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 22

FLUORIDE EMISSION RATES

SAMPLE 102

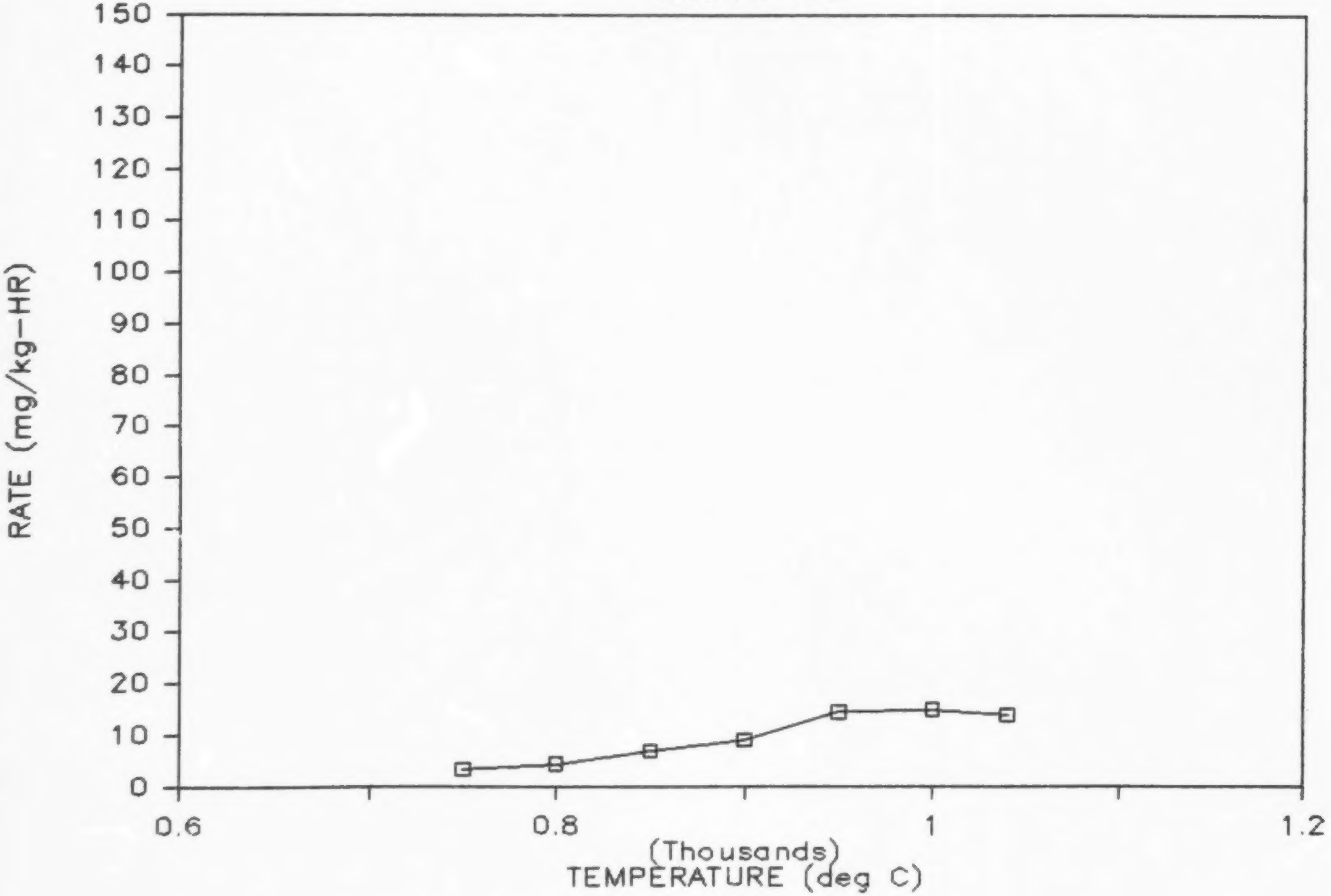
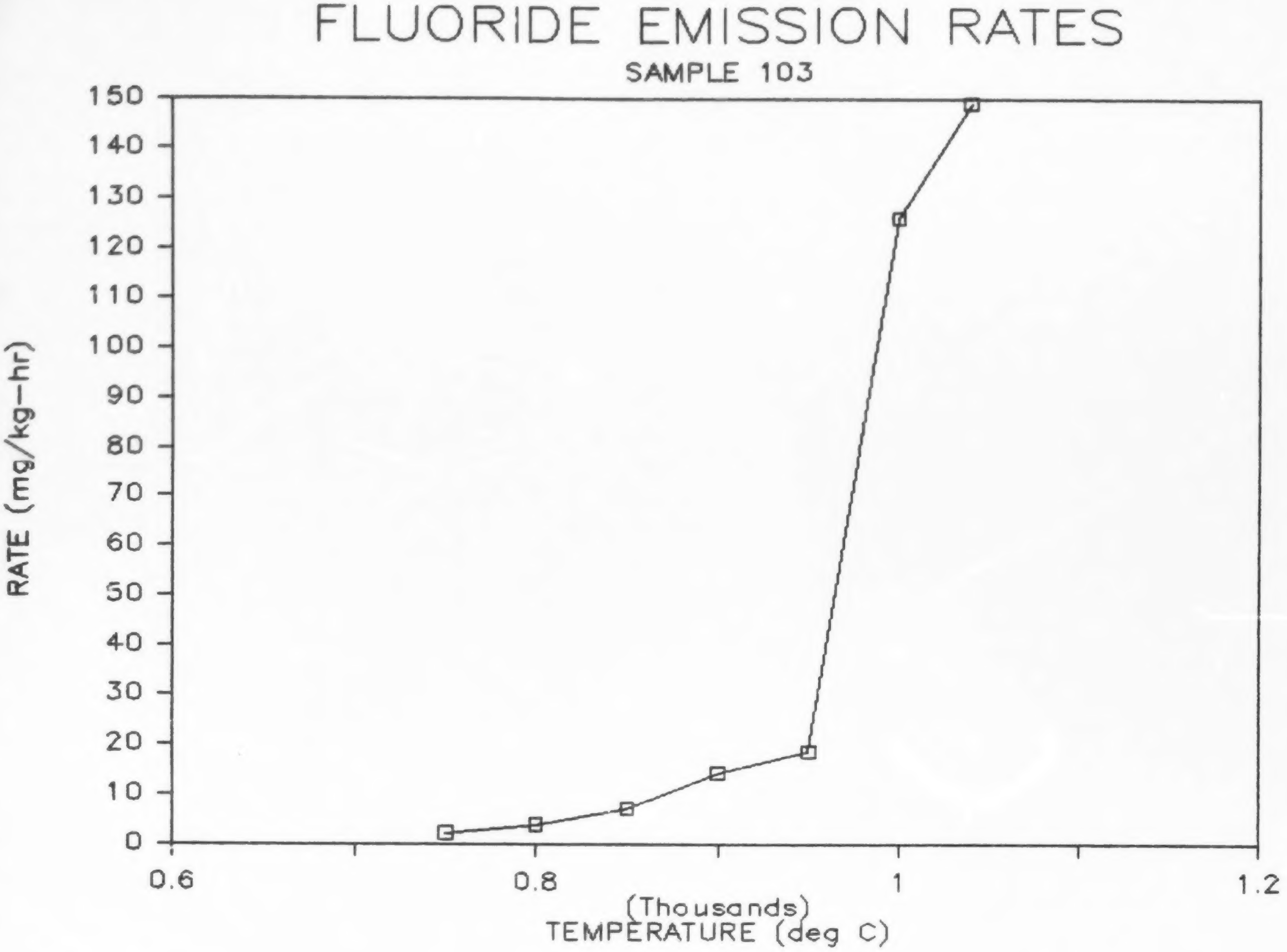


FIGURE 23



FLUORIDE EMISSION RATES

SAMPLE 103

FIGURE 24

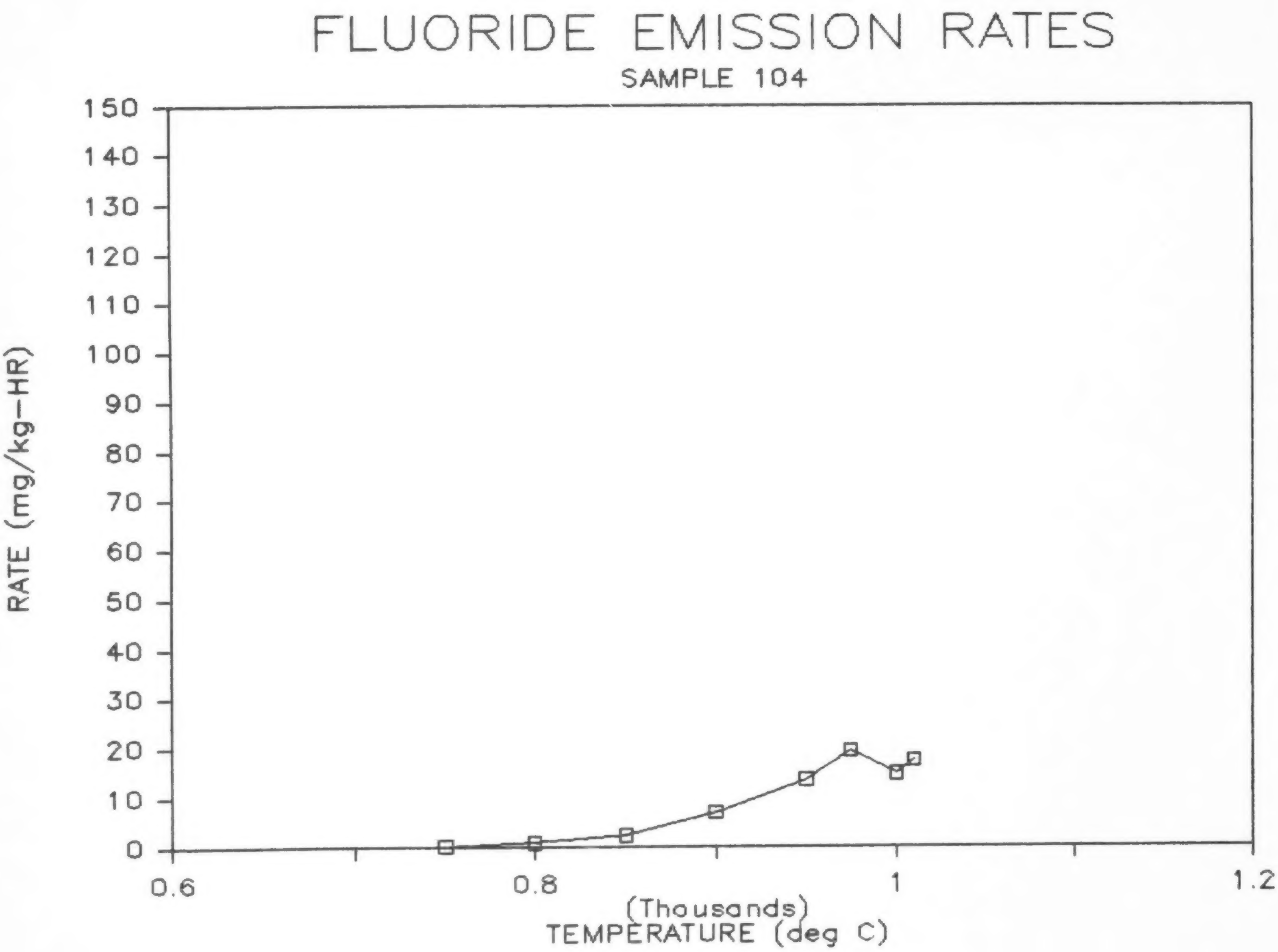

FLUORIDE EMISSION RATES
SAMPLE 104
RATE (mg/kg–HR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 25

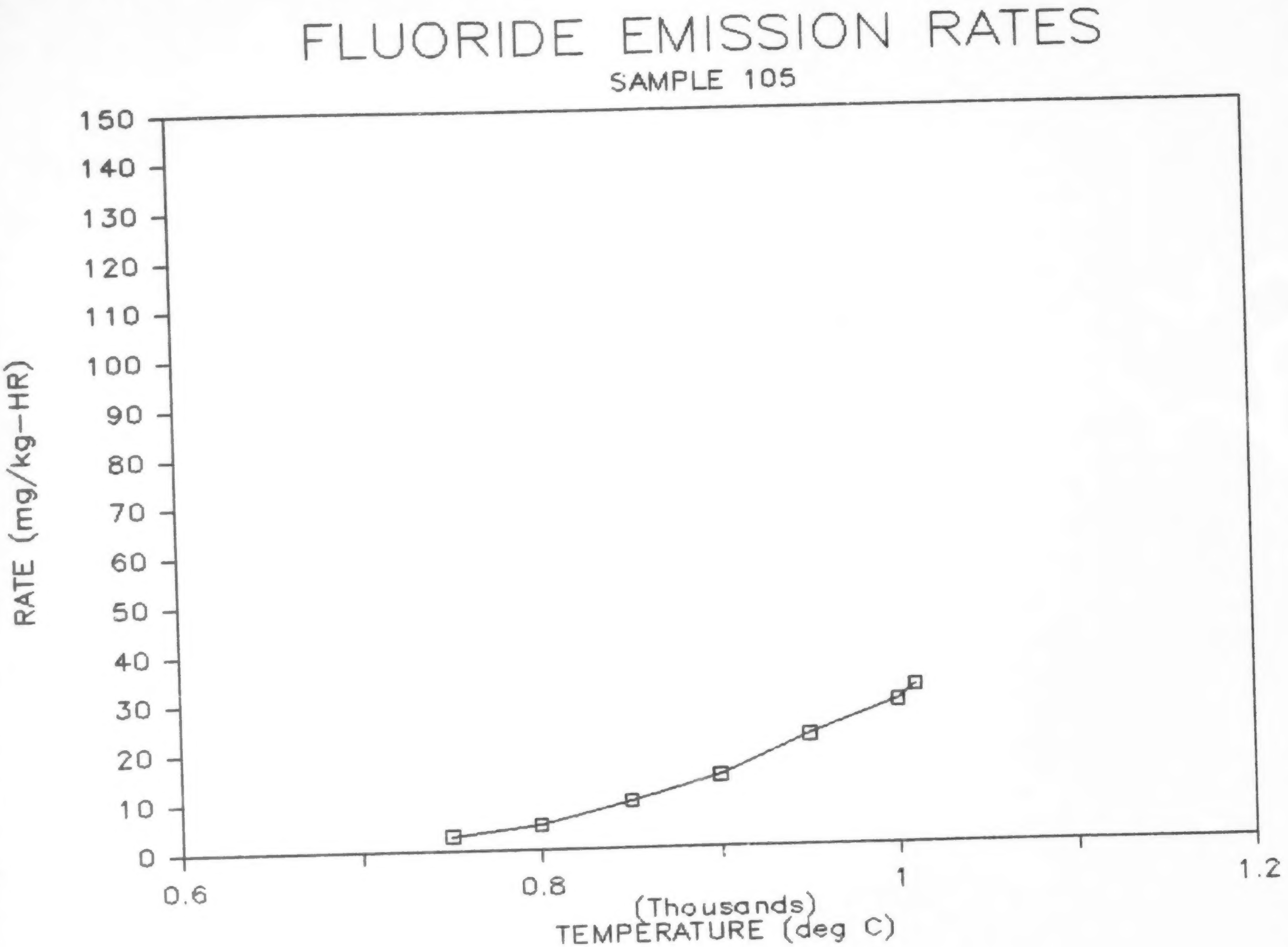

FLUORIDE EMISSION RATES
SAMPLE 105
RATE (mg/kg-HR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 26

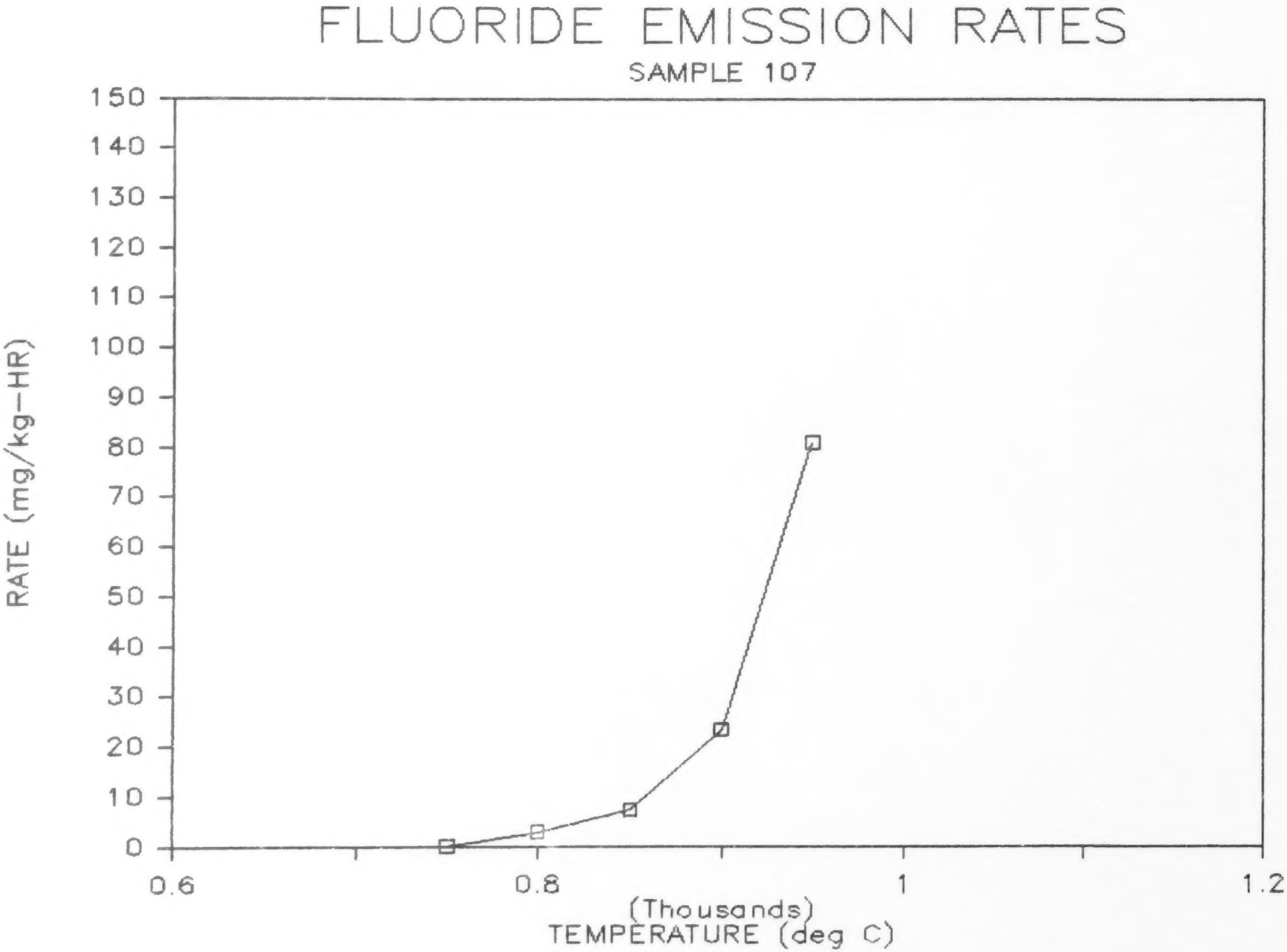
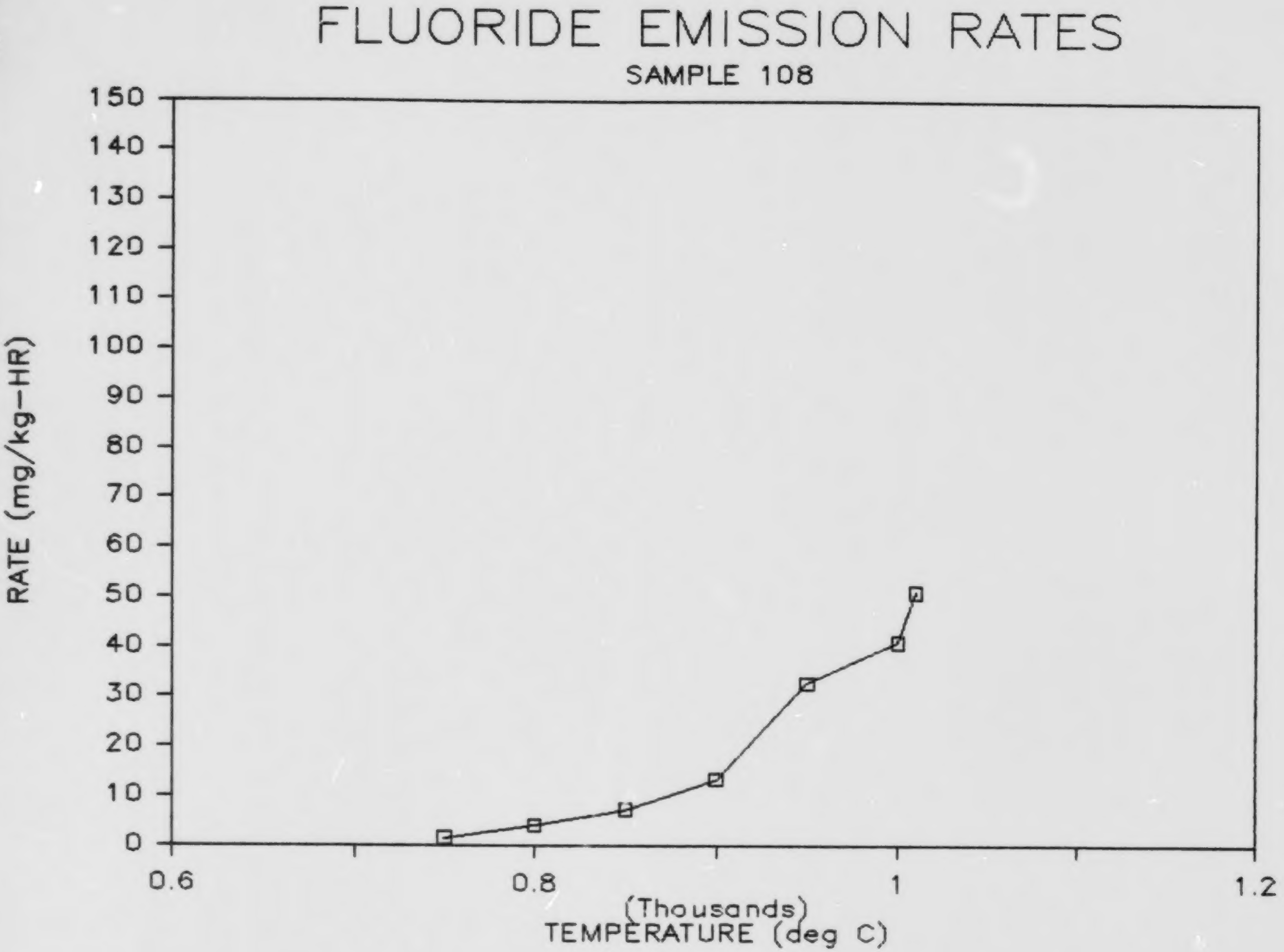

FLUORIDE EMISSION RATES
SAMPLE 107
RATE (mg/kg-HR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 27


FLUORIDE EMISSION RATES

SAMPLE 108

FIGURE 28

FLUORIDE EMISSION RATES

SAMPLE 109

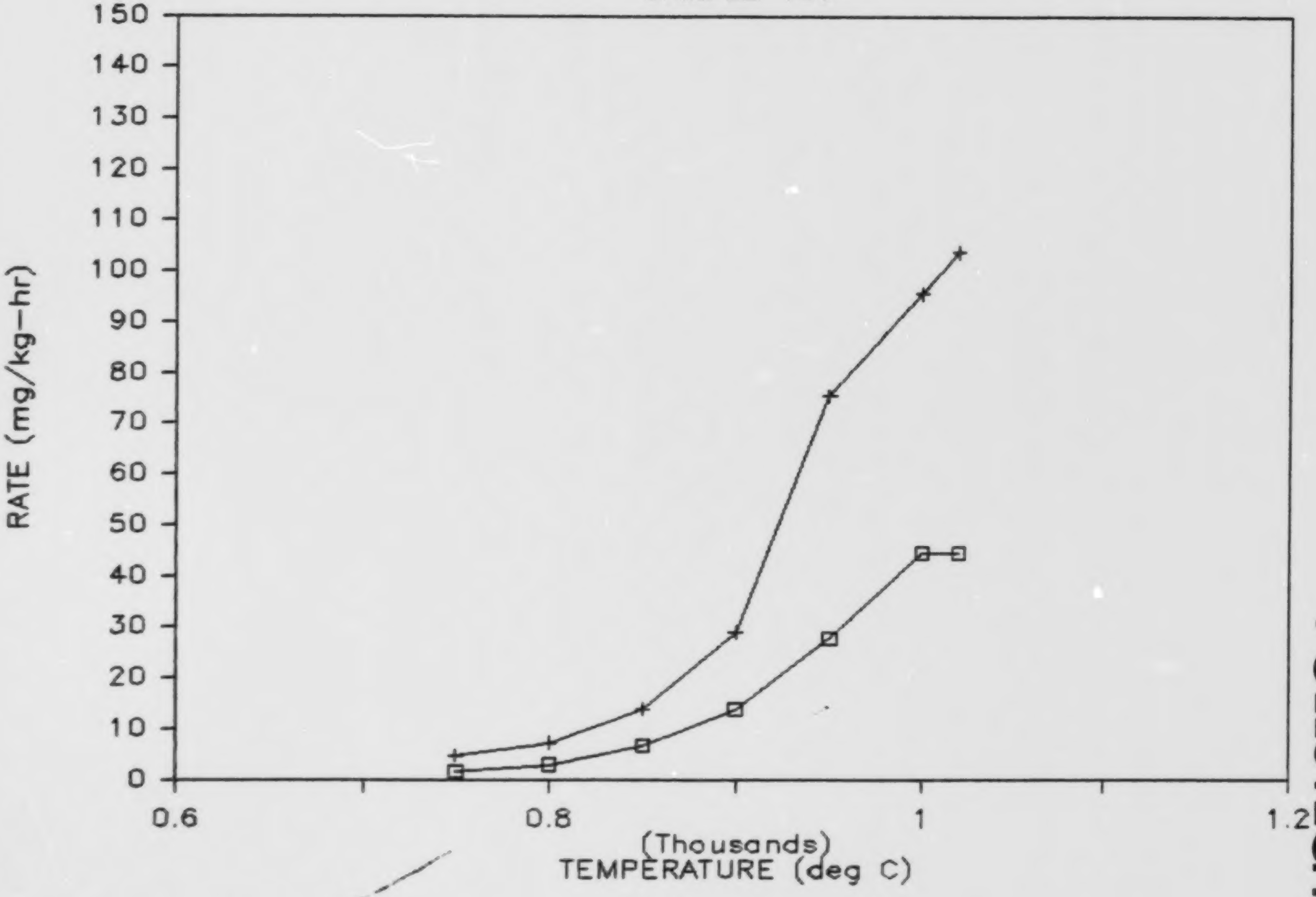


FIGURE 29

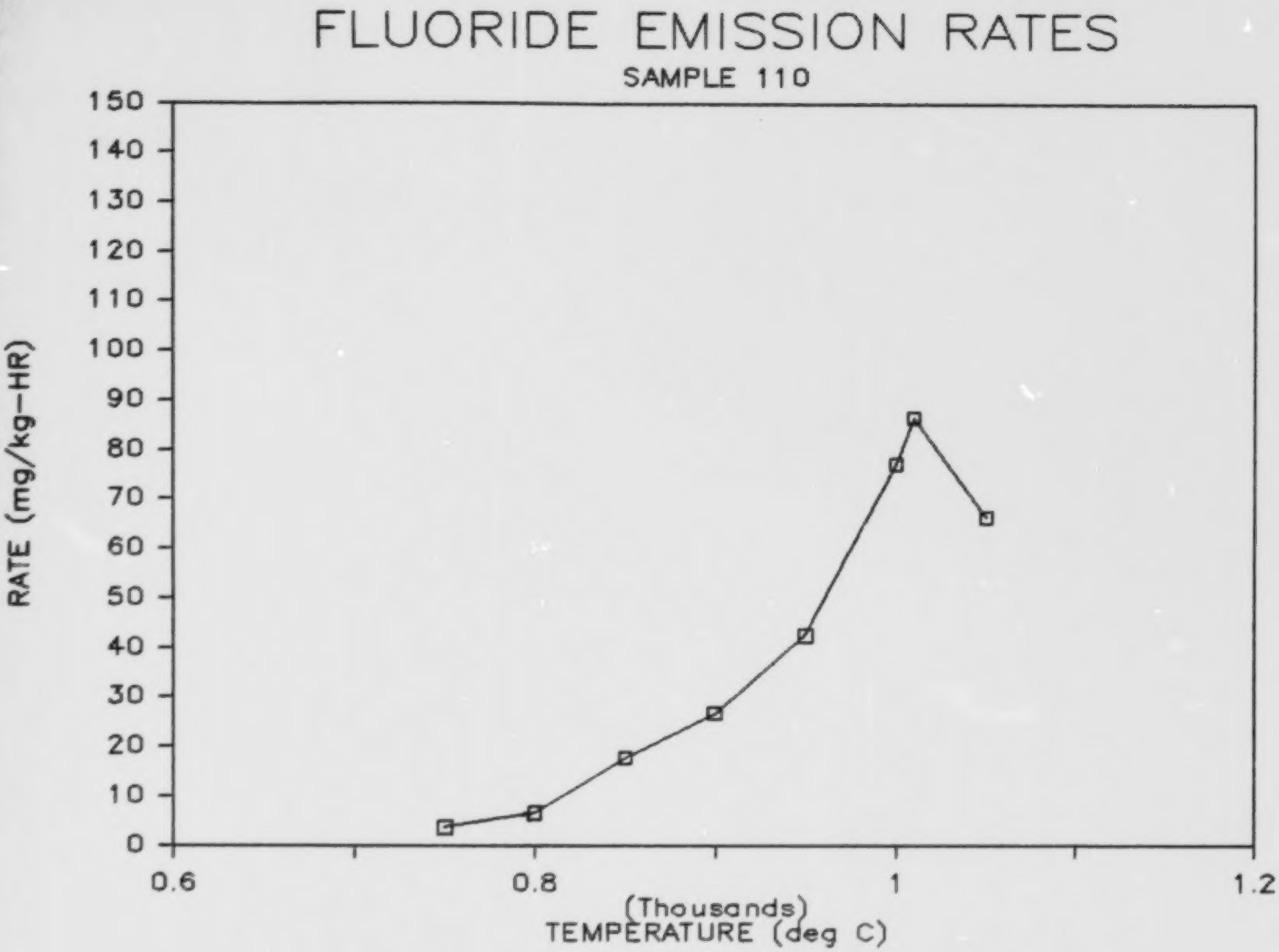

FLUORIDE EMISSION RATES
SAMPLE 110
RATE (mg/kg-HR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 30

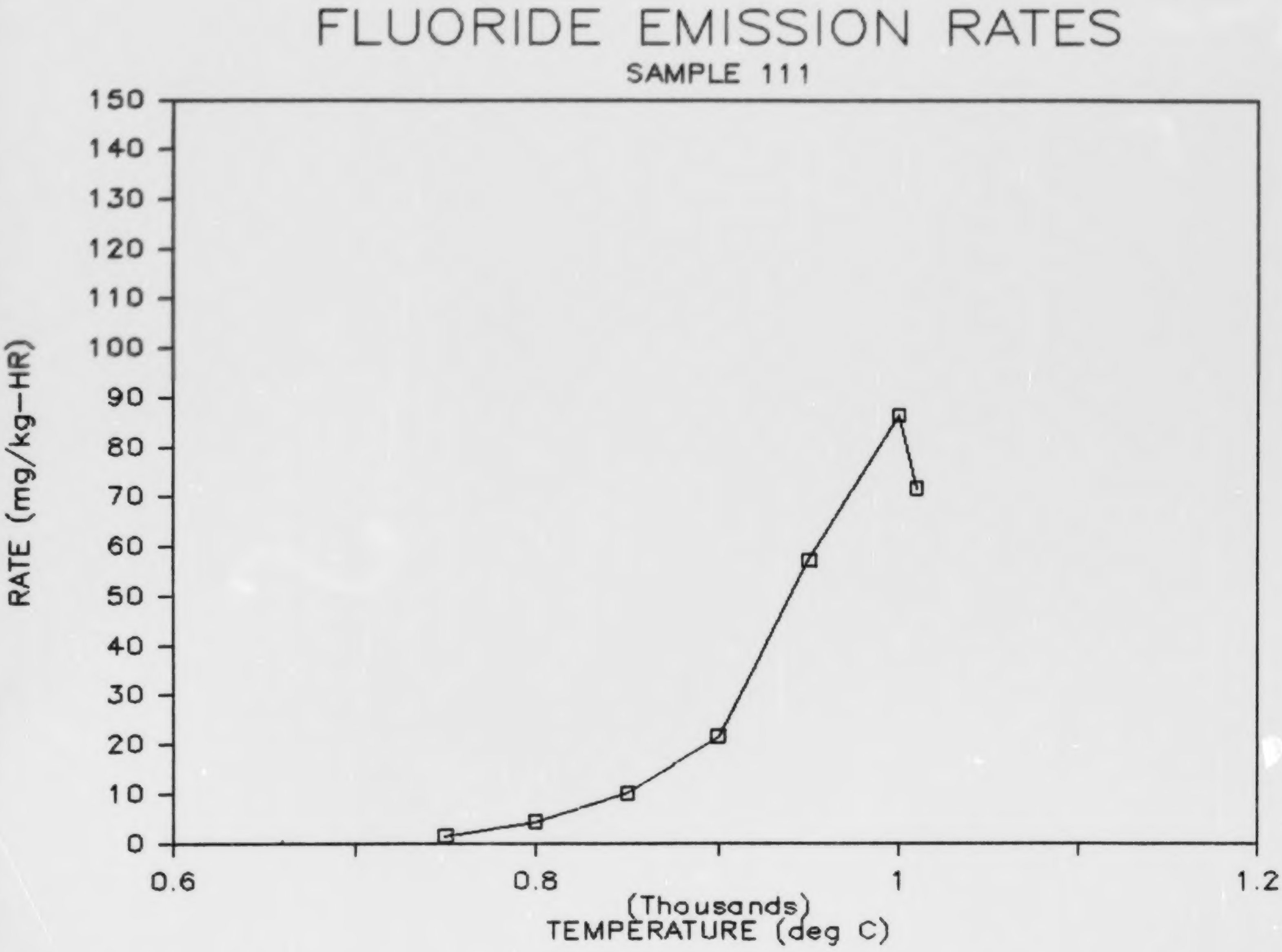
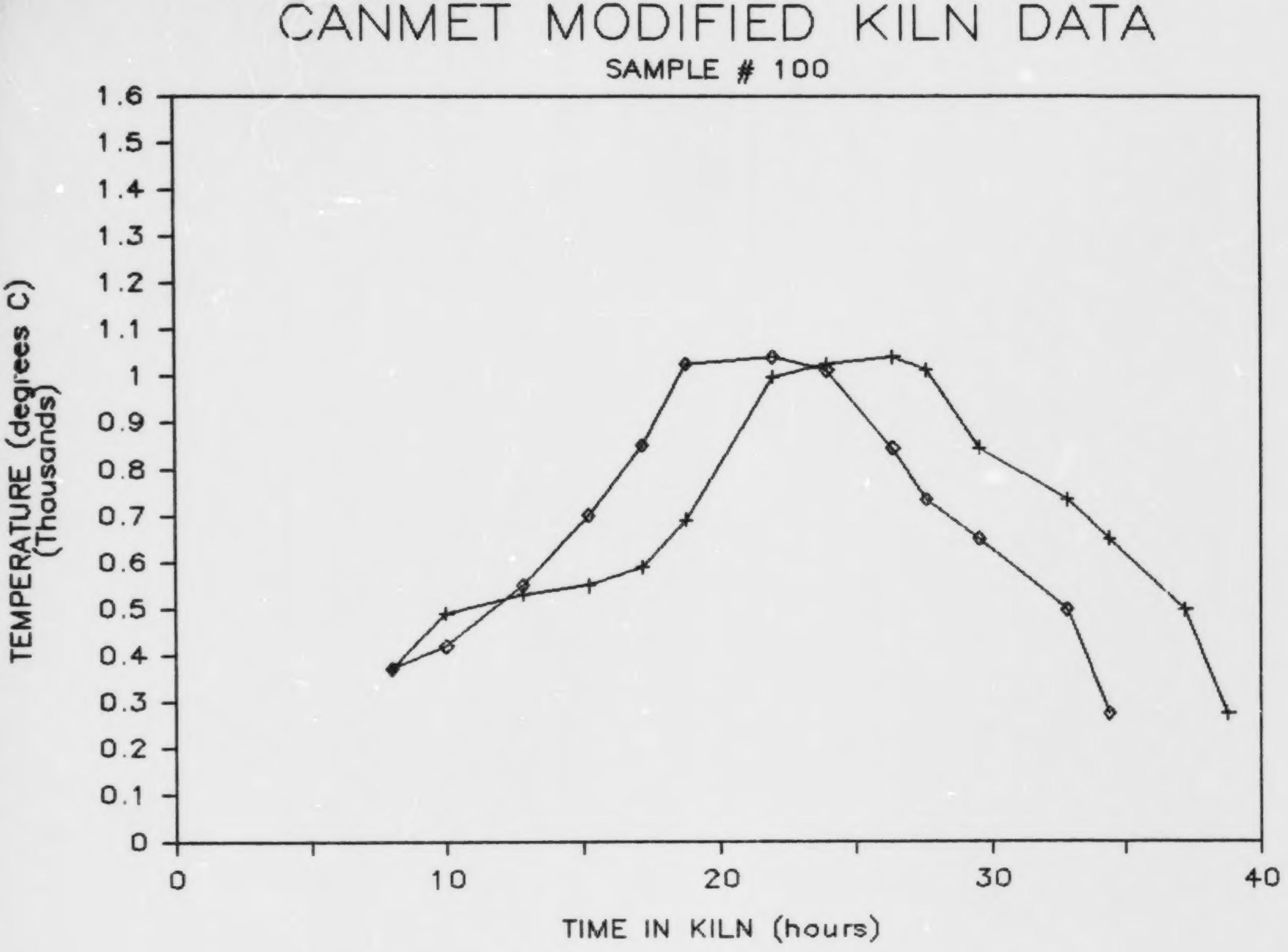

FLUORIDE EMISSION RATES
SAMPLE 111
RATE (mg/kg-HR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0.6
0.8
1
1.2
(Thousands)
TEMPERATURE (deg C)

FIGURE 31



CANMET MODIFIED KILN DATA

SAMPLE # 100

FIGURE 32

CANMET MODIFIED KILN DATA

SAMPLE # 102

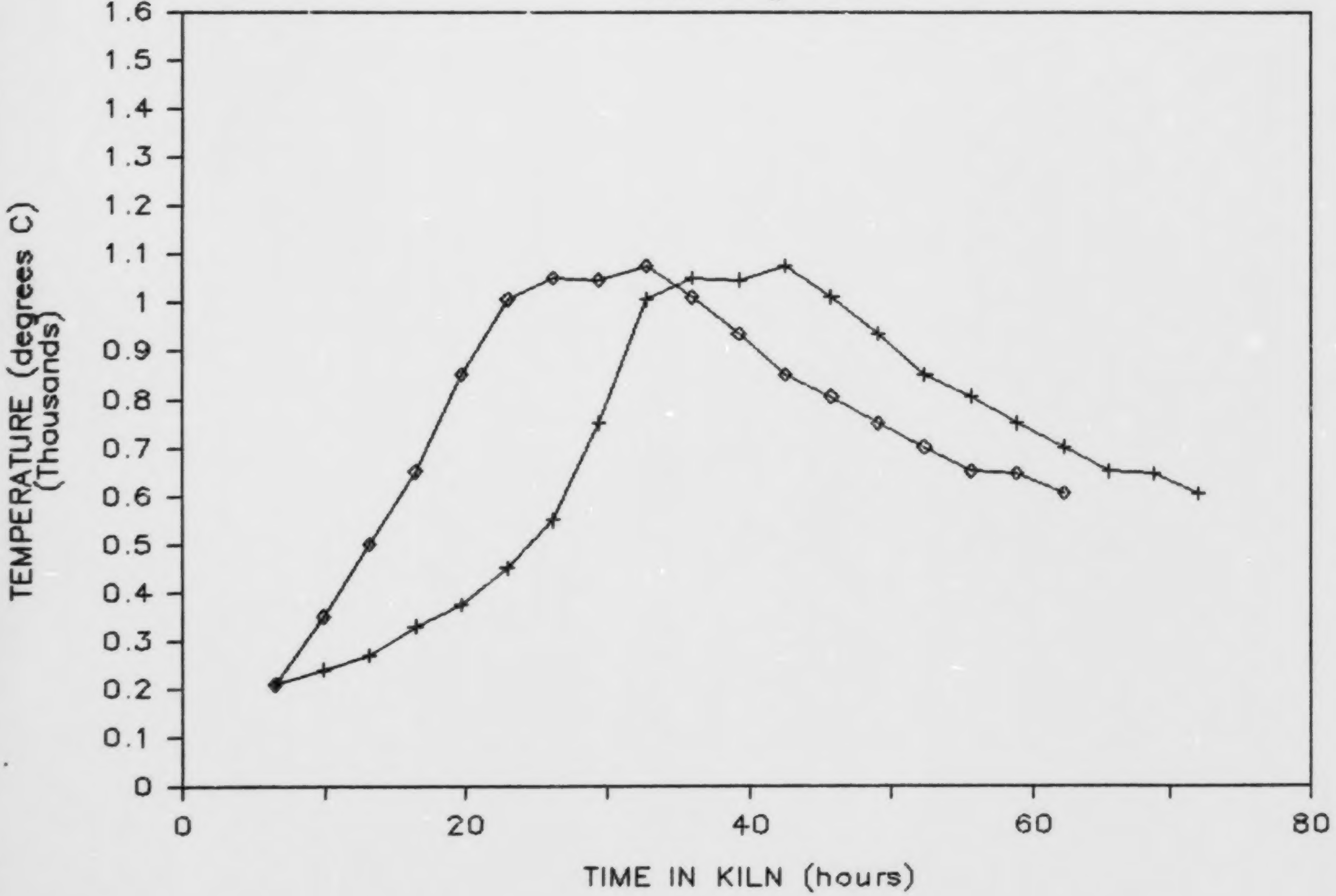


FIGURE 33

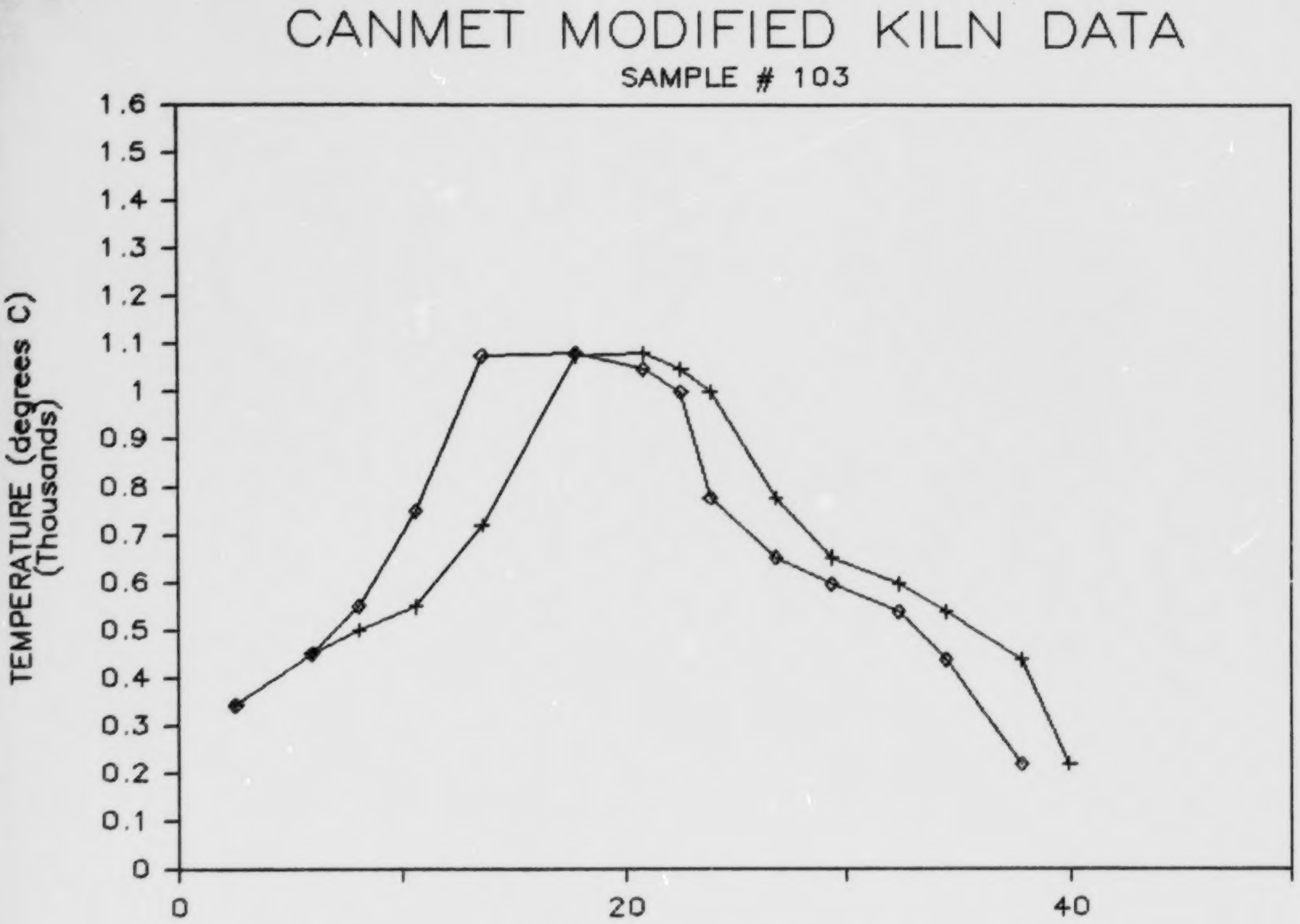
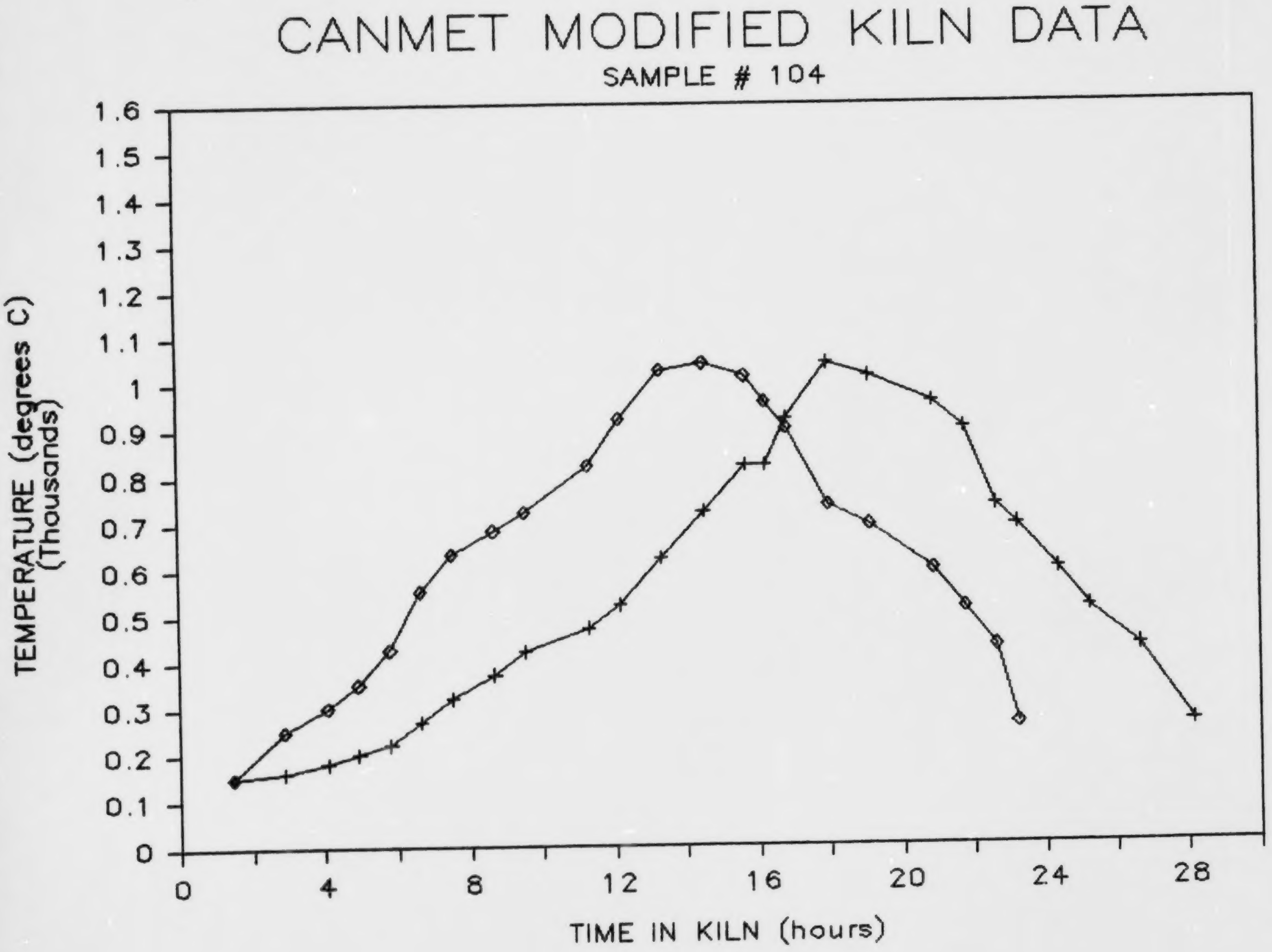
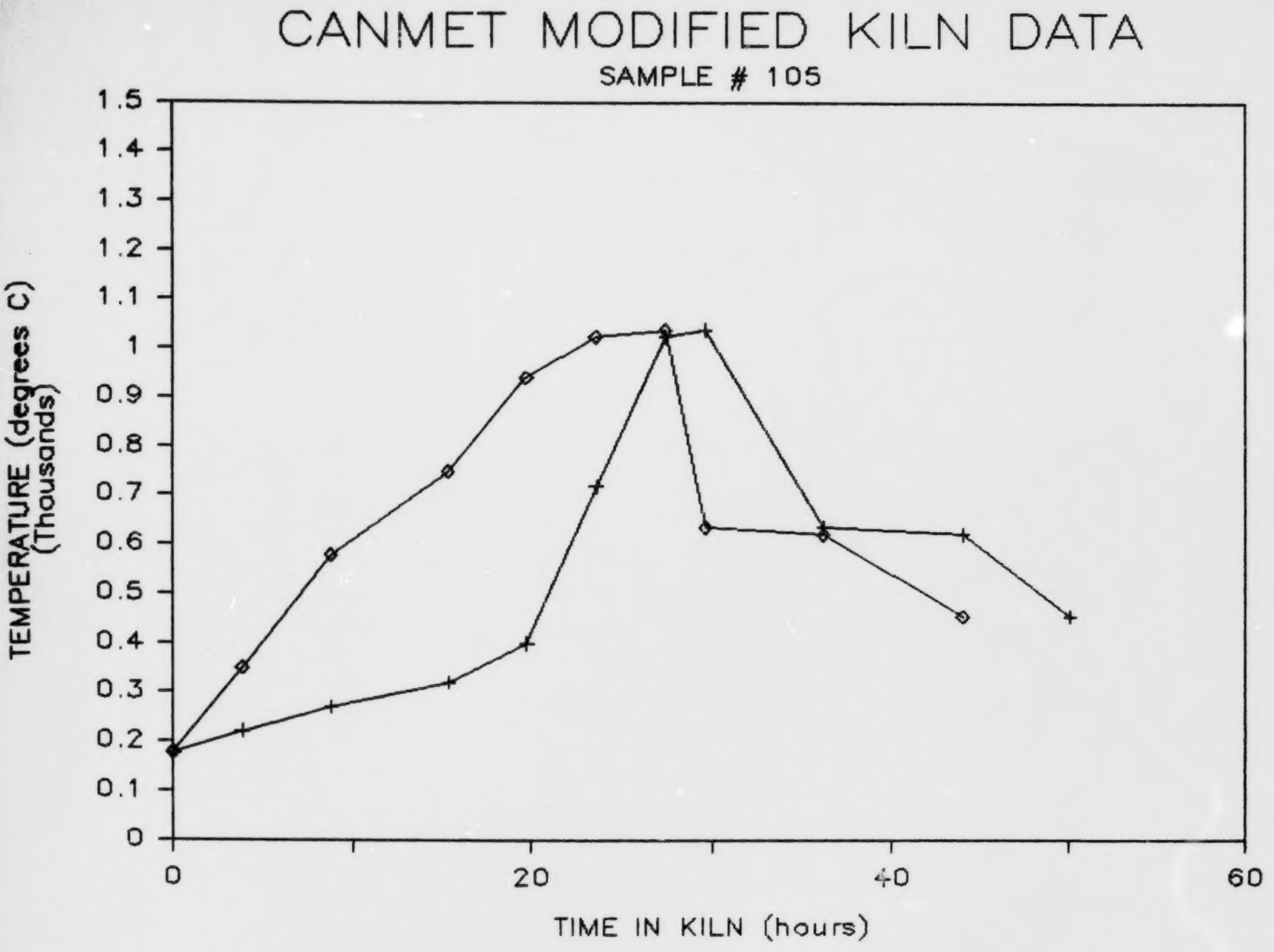

CANMET MODIFIED KILN DATA
SAMPLE # 103
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 34


CANMET MODIFIED KILN DATA

SAMPLE # 104

FIGURE 35



CANMET MODIFIED KILN DATA

SAMPLE # 105

FIGURE 36

POLLUTECH

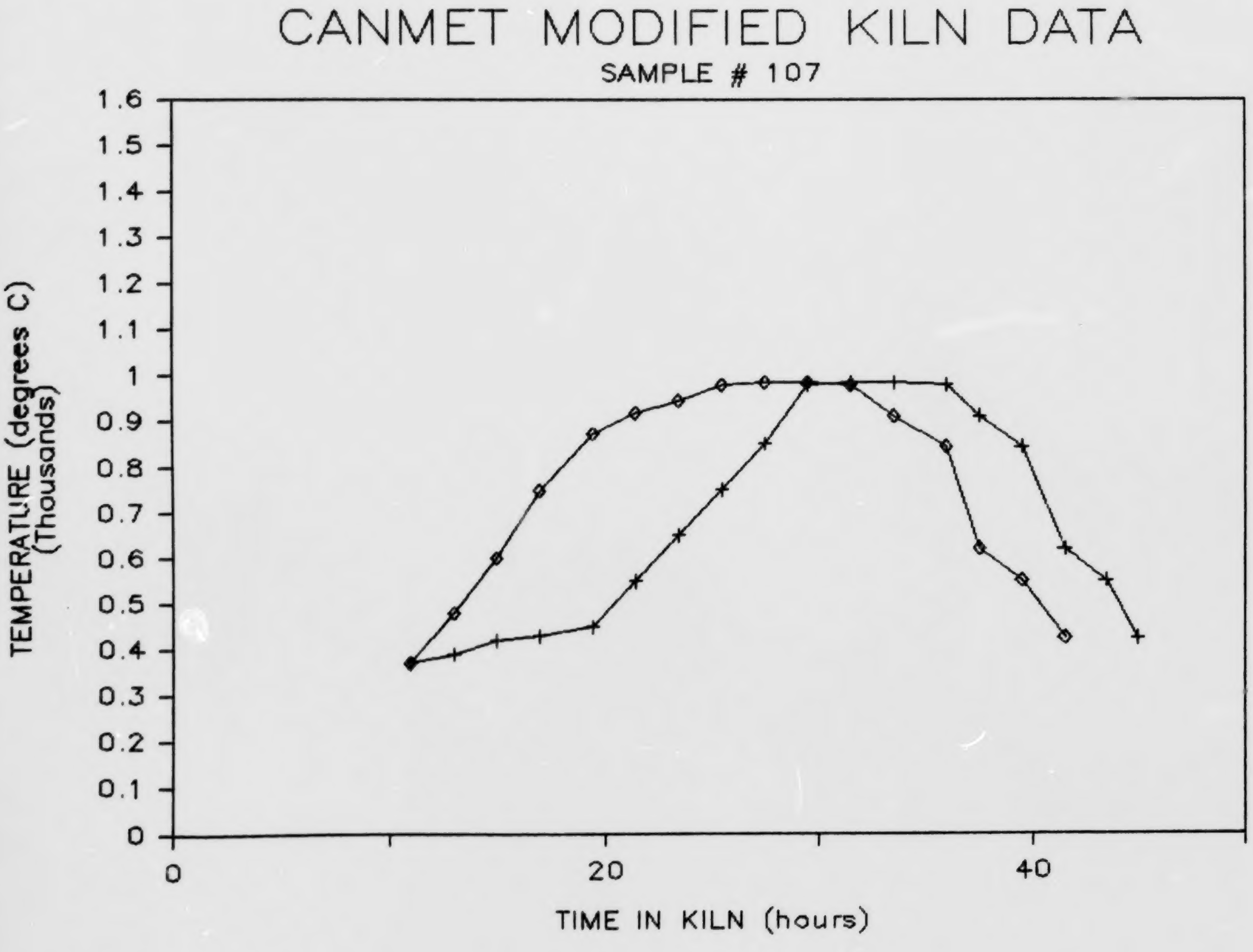

CANMET MODIFIED KILN DATA
SAMPLE # 107
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 37

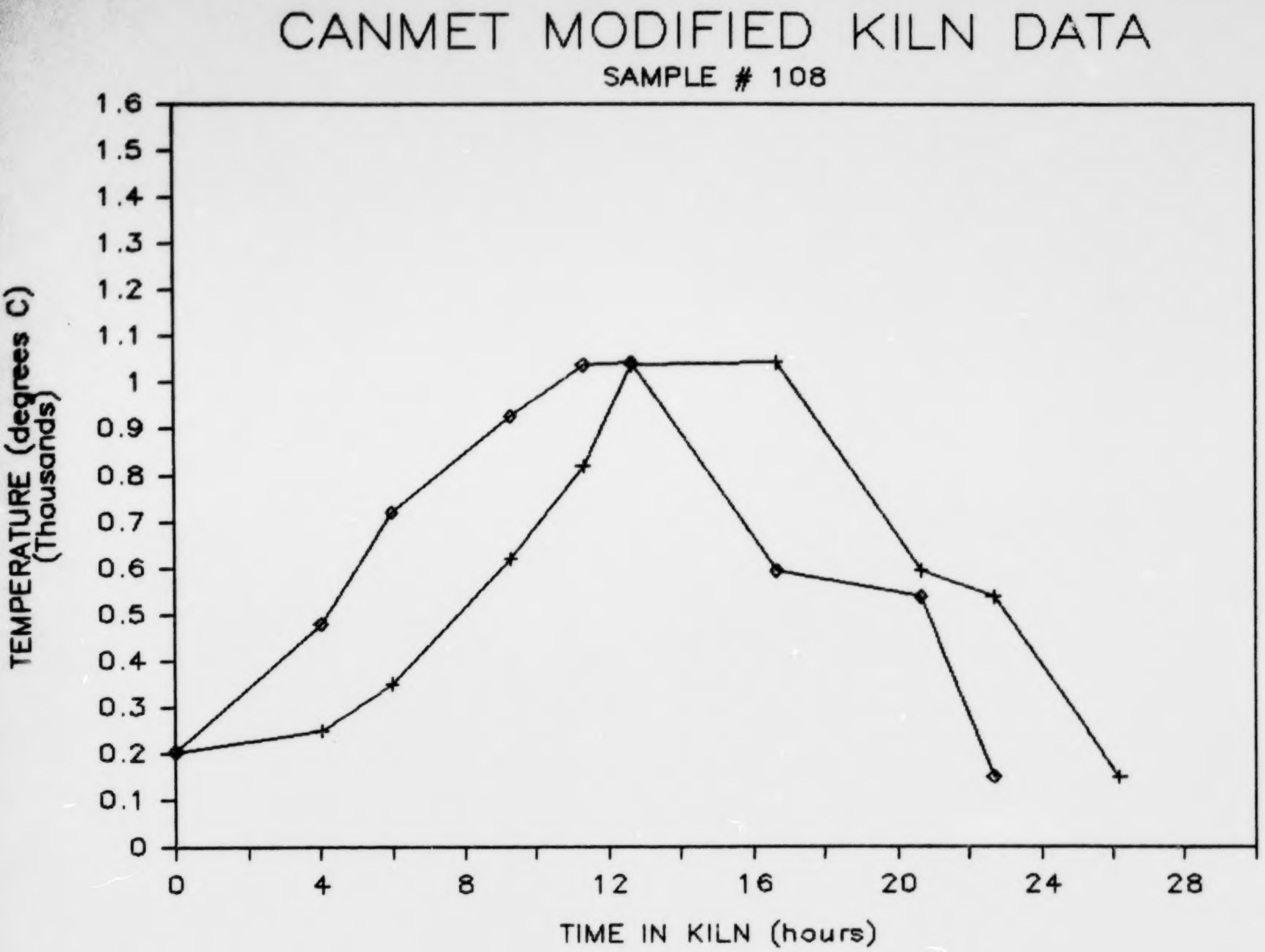

CANMET MODIFIED KILN DATA
SAMPLE # 108
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
4
8
12
16
20
24
28
TIME IN KILN (hours)

FIGURE 38

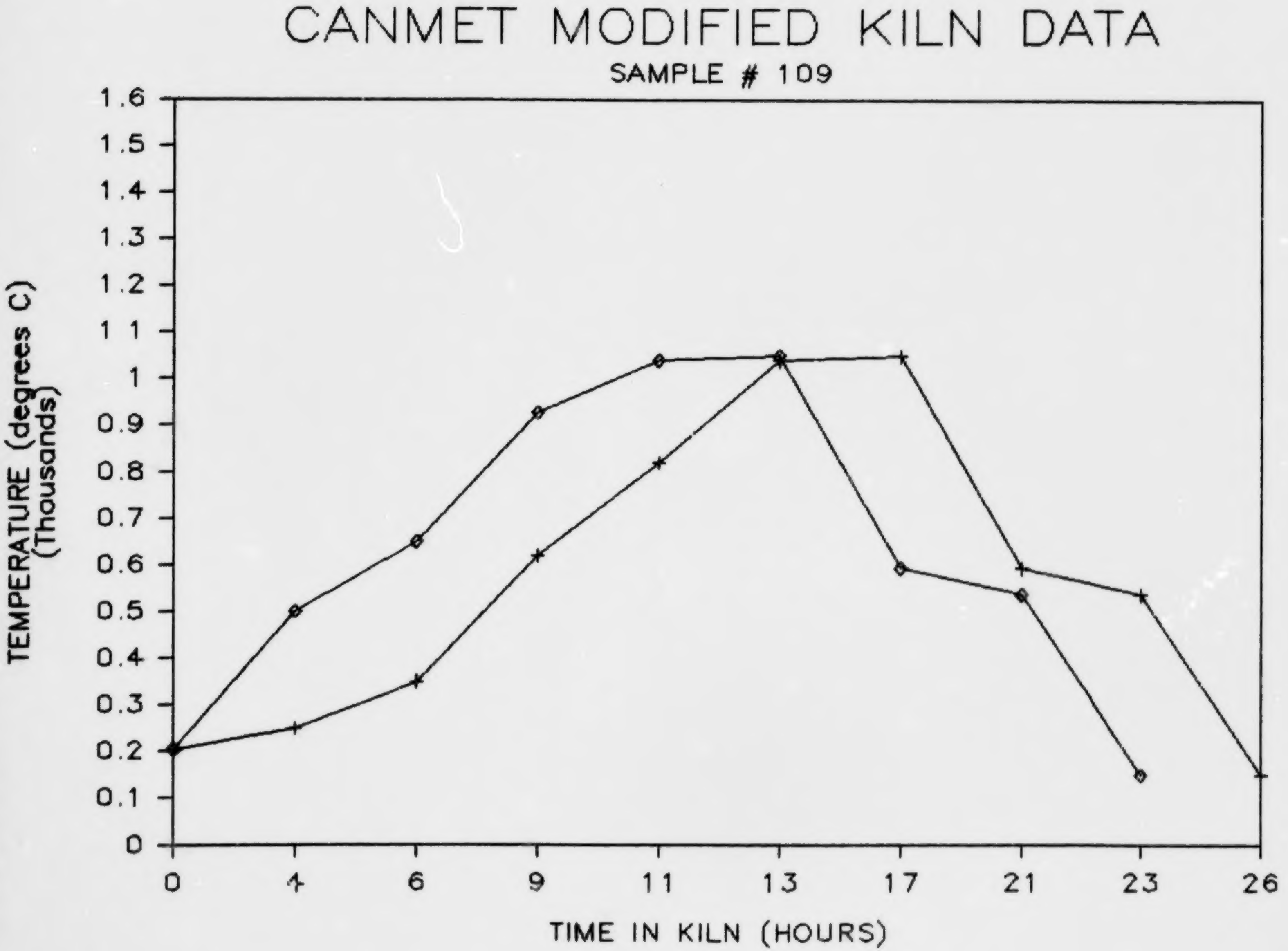

CANMET MODIFIED KILN DATA
SAMPLE # 109
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
4
6
9
11
13
17
21
23
26
TIME IN KILN (HOURS)

FIGURE 39

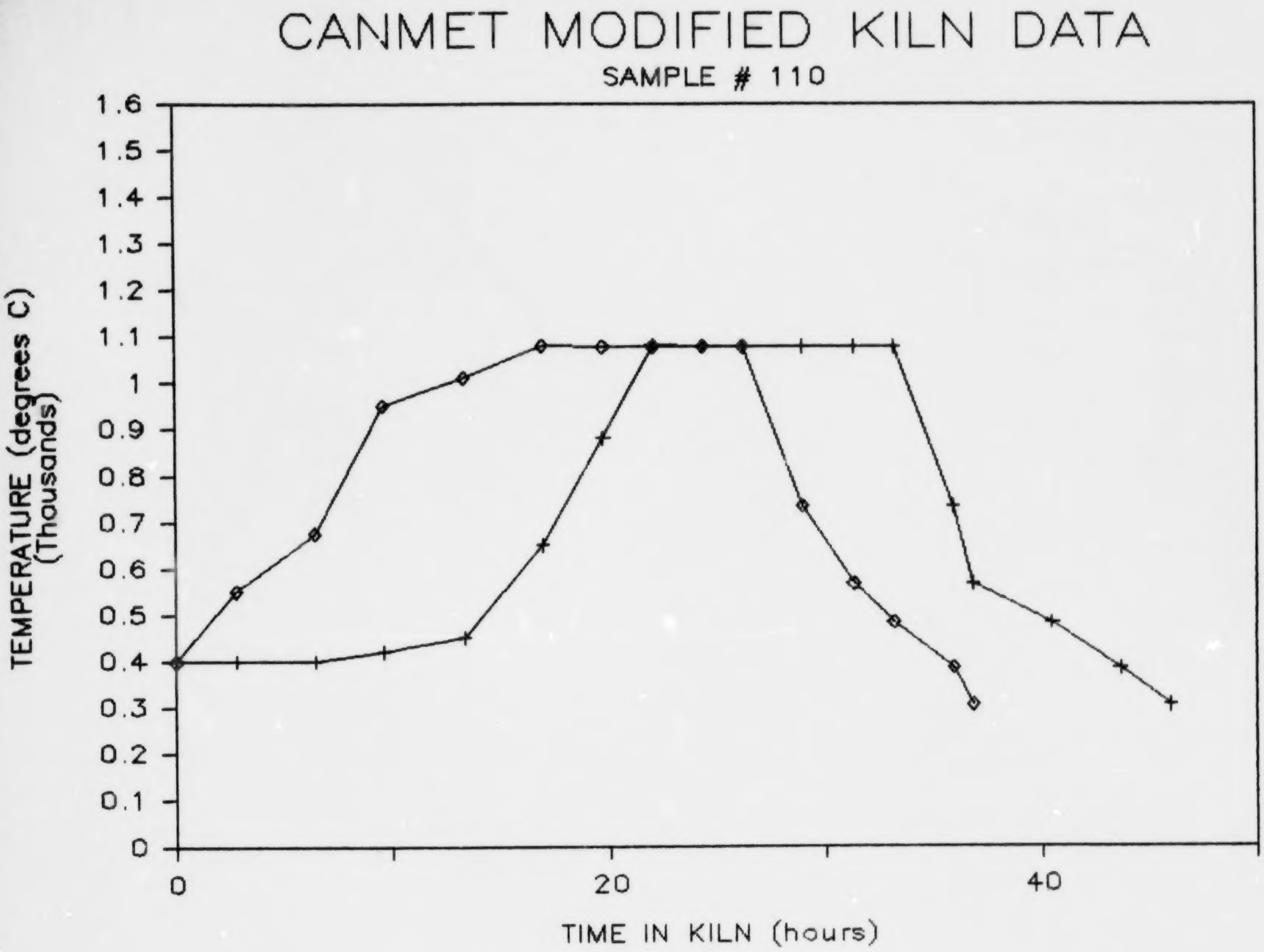

CANMET MODIFIED KILN DATA
SAMPLE # 110
TEMPERATURE (degrees C)
(Thousands)
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
TIME IN KILN (hours)

FIGURE 40

CANMET MODIFIED KILN DATA

SAMPLE # 111

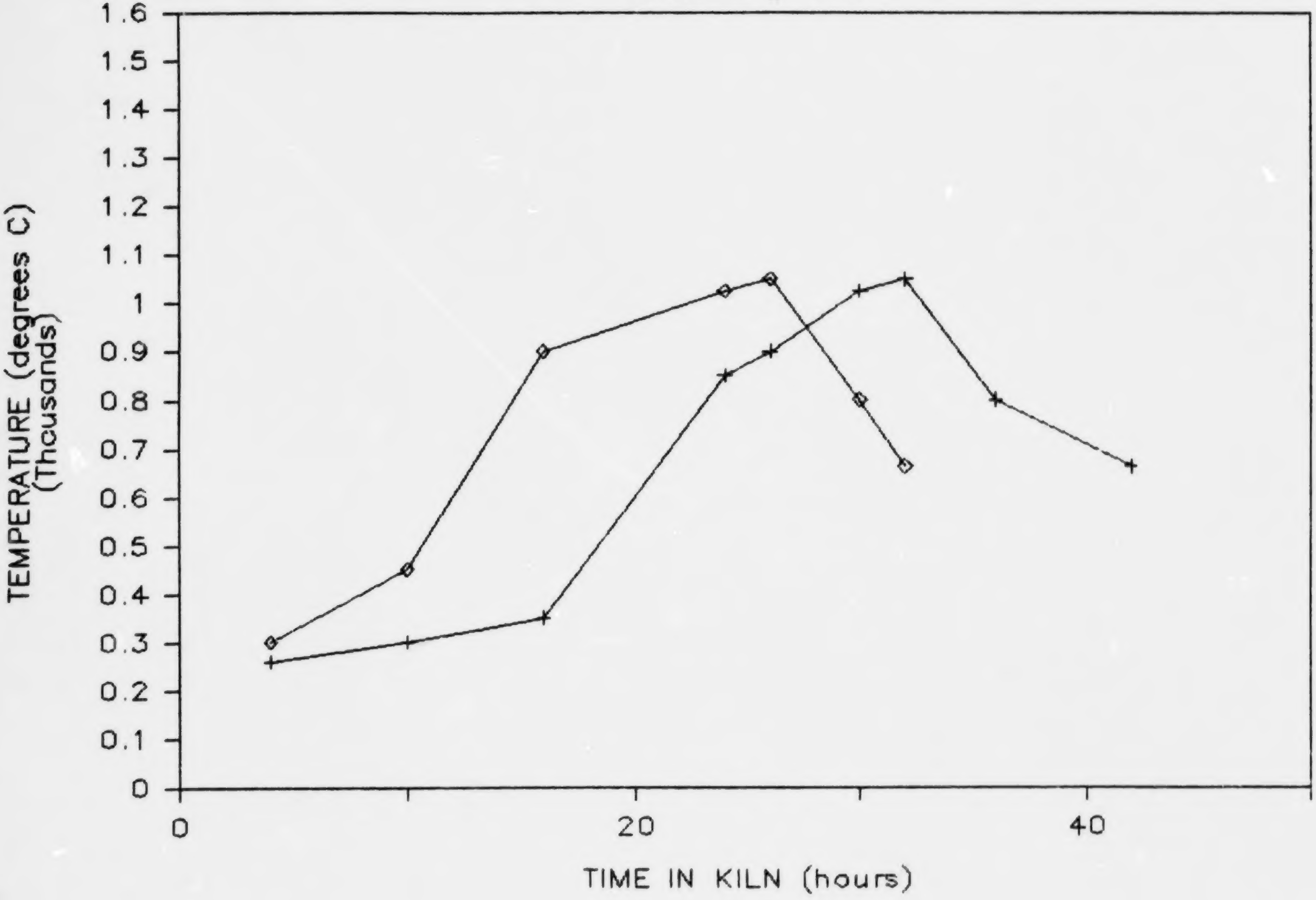


FIGURE 41

POLLUTECH

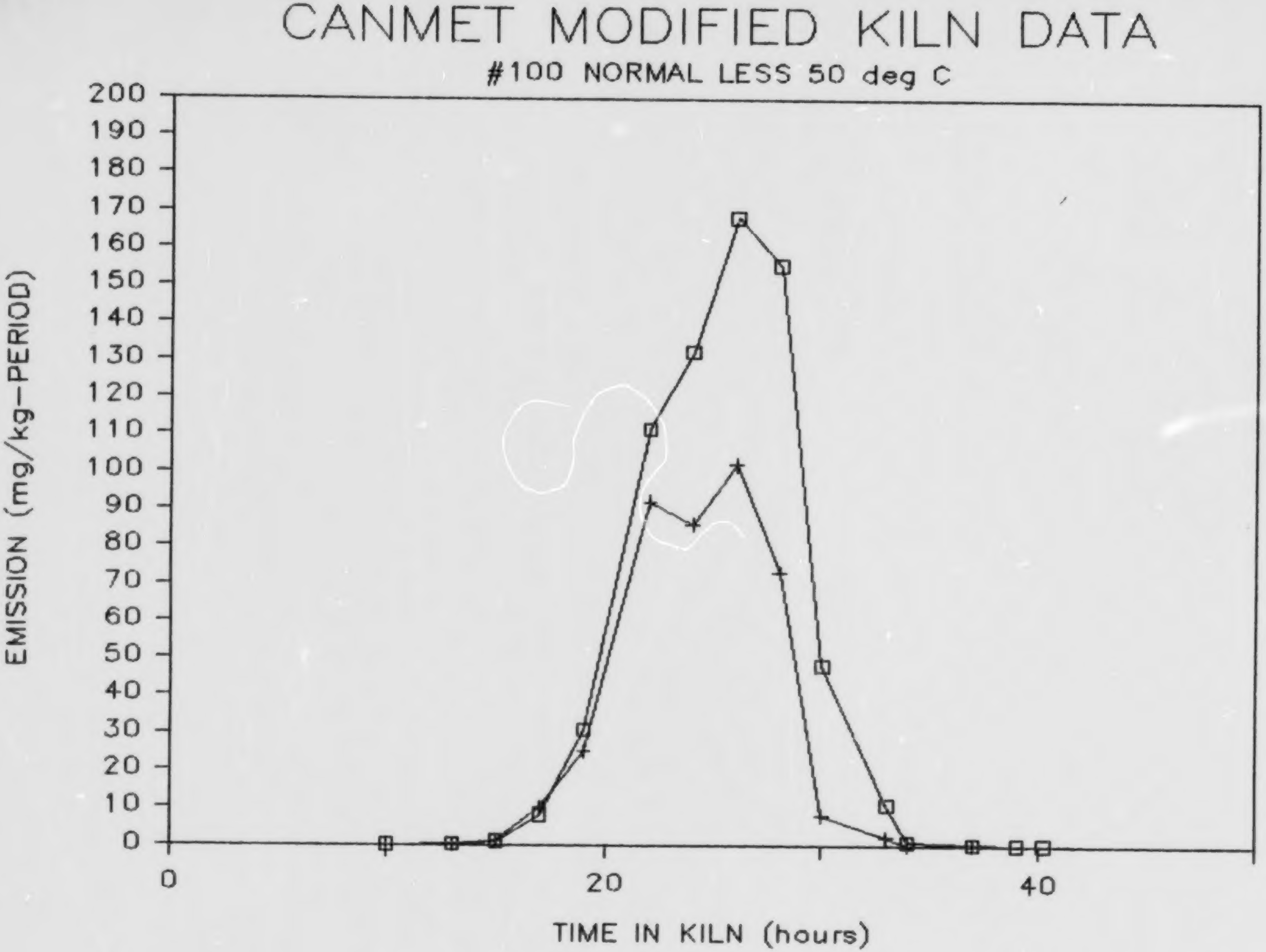

CANMET MODIFIED KILN DATA
#100 NORMAL LESS 50 deg C
EMISSION (mg/kg–PERIOD)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
TIME IN KILN (hours)

FIGURE 42

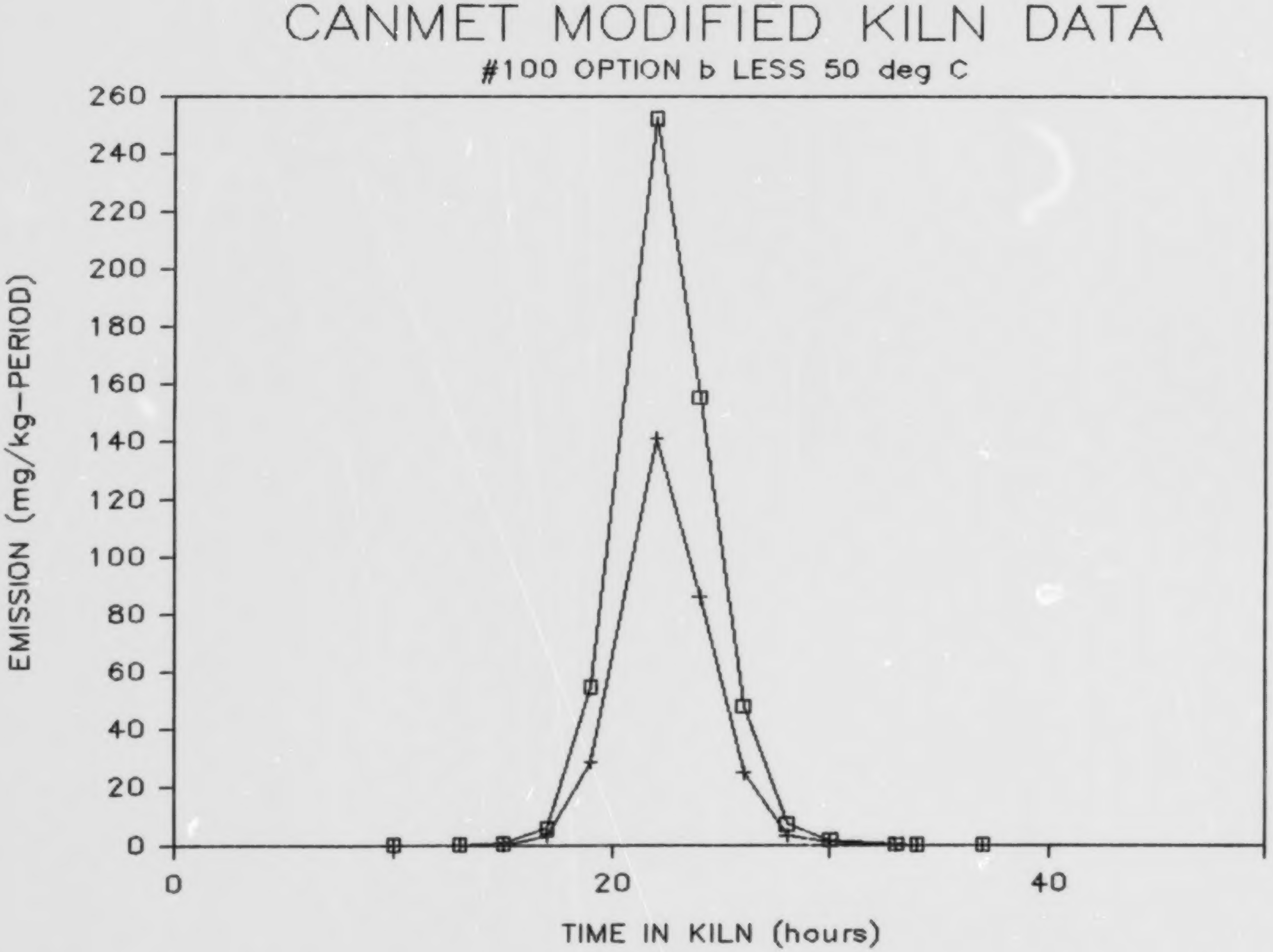

CANMET MODIFIED KILN DATA
#100 OPTION b LESS 50 deg C
EMISSION (mg/kg-PERIOD)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
20
40
TIME IN KILN (hours)

FIGURE 43

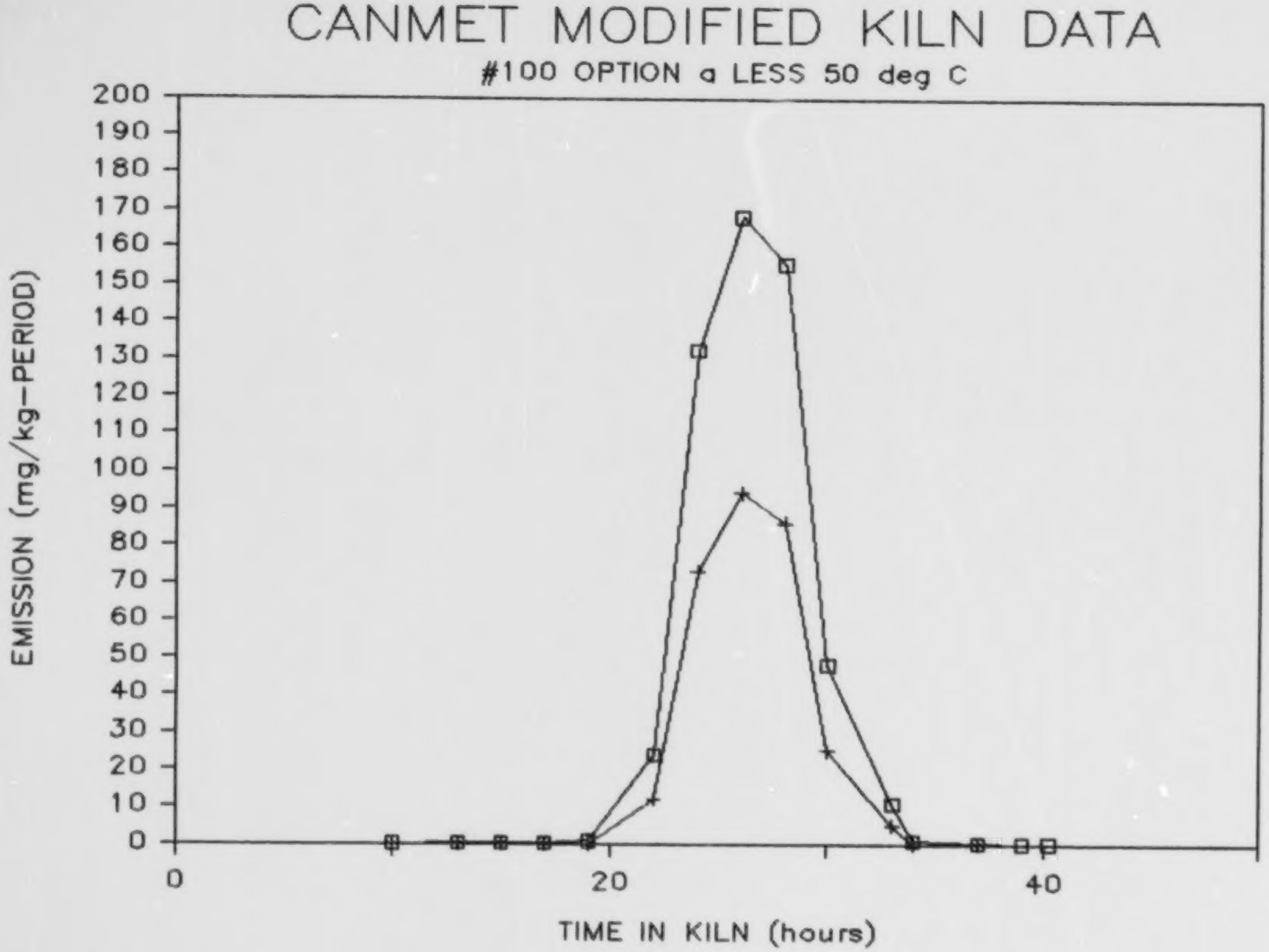

CANMET MODIFIED KILN DATA
#100 OPTION a LESS 50 deg C
EMISSION (mg/kg-PERIOD)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
TIME IN KILN (hours)

FIGURE 44

APPENDICES

- References
- Plant Operating Data

APPENDIX 1

References

References

1. Troll, G. and Farzaneh, A., "Fluorine Loss in Production of Bricks and Comparison with the Loss in Fluorine-bearing Minerals", Interceram, Vol. 27, No. 3, p. 300, 1978.

2. Luxon, S.G., "Fluoride Emission During Firing of Pottery in Continuous Kilns", Fluoride Vol. 3, p. 61, 1970.

3. Tunker, G. and Schmidt, H., "Solution to a Fluorine Emission Problem in Stoneware Production", Ziegelindustrie Int. 3, p. 173, 1982.

4. Kother, W. and Pauls, N., "Determination of a Production Firing Curve for Optimum Fluorine Bonding in Brick Firing", Ziegelindustrie Int. 3 p. 167, 1982.

5. Routschka, G., Buttgerist, C. and Berger, U., Sprechsaal 103 901, 1970.

6. Routschka, C. and Majdic, A., "Studies on the Behavious of Fluoride in the Firing of Refractory Clays", Ziegelindustrie Int. No. 4, p.227, 1979.

7. Routschka, C. and Majdic, A., "Fluoride Emission in the Kiln Firing of Refractory Clays to Chamotte", Ziegelindustrie Int. No. 1, p. 6, 1978.

8. Smidt, H., "Fluoride - central problem for the brick and tile industry in the sector of clearn air", Ziegelindustrie Int. No. 4, p. 165, 1977.

APPENDIX 2

Plant Operating Data

Brick Plant A

- Chemical Analysis

ANALYSIS	PERCENT A	PERCENT B
SiO_2	55.74	63.14
Al_2O_3	19.13	14.75
Fe_2O_3	7.32	5.27
K_2O	3.25	2.40
CaO	2.12	2.48
MgO	2.46	1.86
TiO_2	0.95	0.82
L.O.I	8.05	6.47

- Physical Properties Data

Compression strength	- 8000 PSI
24-hour cold adsorption	- not given
Five hour boiling test	- 6.0 %
Saturation coefficient (C/B)	- 0.60

- Production
  - 30 x 10^6 brick units/year

- Fuel Consumption
  - 2250 BTU/lb (includes drying)

Brick Plant B

- Chemical Analysis (data not provided)
- Physical Properties Data (data not provided)
- Production
    - 200 tons/day
- Fuel Consumption
    - 1050 BTU/lb

Brick Plant C

- Chemical Analysis

ANALYSIS	PERCENT
SiO_2	65.8
Al_2O_3	13.9
Fe_2O_3	5.2
MnO	0.07
CaO	7.3
MgO	2.3
Na_2O	0.80
K_2O	2.30

- Physical Properties Data

  Compression strength - 5086 PSI
  24-hour cold adsorption - 9.8%
  5-hour Boiling Test - 11.7%
  Saturation Coefficient (C/B) - 0.84

- Production
  - 31 x 10^6 brick units/year
  - 170 ton/day

- Fuel Consumption
  - 1300 BTU/lb

Brick Plant D

- Chemical Analysis

ANALYSIS	PERCENT
SiO_2	55.6
Al_2O_3	14.4
Fe_2O_3	6.2
K_2O	3.6
CaO	5.2
MgO	2.8
Na_2O	1.0
MgO	2.8

- Physical Properties Data

Compression Strength	- 12,791
24-hour cold adsorption	- 5.9
5-hour boiling test	- 7.8
Saturation Coefficient (C/B)	- 0.75

- Production
  - 470 tons/day

- Fuel Consumption
  - 981 BTU/lb

Brick Plant E

- Chemical Analysis

    - the breakdown of the raw product chemical composition was not provided by plant operations staff, however they did indicate that the product is approximately 22 percent SiO_2 and other major constituents which were AL_2O_3, Fe_2O_3, and water

- Physical Properties Data

Compression strength	- 10,000 PSI
24-hour cold absorption	- 6%
5 hour boiling test	- 8%
Saturation coefficient (C/B)	- 0.79

- Production
    - 165 tons/day

- Fuel Consumption
    - 990 BTU/lb

Brick Plant F

- Chemical Analysis

ANALYSIS	PERCENT A	PERCENT B
SiO_2	62.43	89.94
Al_2O_3	17.33	6.52
Fe_2O_3	2.49	2.40
MnO	0.01	-
CaO	0.38	-
MgO	0.80	0.93
Na_2O	0.41	1.30
K_2O	3.00	-
TiO_2	0.84	-
P_2O_5	0.12	-
LOI	9.60	7.78
C	2.1	Trace
SO_3	-	0.16

- Physical Properties Data

Compressive strength	- 5238 PSI
24-hour cold adsorption	- 6.72%
5-Hour boiling test	- 10.43%
Saturation Coefficient (C/B)	- 0.64

- Fuel Consumption
  - 1700 BTU/pound fired ware
  - 9.51×10^6 BTU/1000 brick units

Brick Plant G

- Chemical Analysis (data not provided)
- Physical Properties Data (data not provided)
- Production
  - 240 tons/day
- Fuel Consumption
  - 1100 BTU/day

Brick Plant H

- Chemical Analysis

ANALYSIS	PERCENT	
	A	B
SiO_2	55.15	58.74
FeO	3.45	1.72
Fe_2O_3	1.72	6.05
TiO_2	0.67	0.85
Al_2O_3	13.39	20.77
CaO	6.84	0.31
MgO	3.53	2.26
Na_2O	1.03	1.14
K_2O	3.08	3.18
LOI	11.12	4.67
S	0.73	0.02
CO_2	5.98	0.01
Quartz	23.30	25.32
Total C	2.21	0.02

- Physical Properties Data

	A	B
24-hour Cold Absorption	7-11%	5-8%

- Production
  - 252 ton/day

- Fuel Consumption
  - 1,350 BTU per pound with "A"
  - 1,550 BTU per pound with "B"

Brick Plant I

- Chemical Analysis

ANALYSIS	COMPONENTS	
	A	B
SiO_2	69.43	62.82
Al_2O_3	14.65	15.36
Fe_2O_3	4.39	5.33
F^-	0.06	0.10
MnO	0.05	0.10
CaO	0.07	1.96
MgO	1.25	2.82
Na_2O	1.38	1.78
K_2O	3.73	3.05
LOI	4.41	5.38

- Physical Properties Data
  - Compressive Strength - 7276 PSI
  - 24-hour cold adsoption - 6.4
  - 5-Hour Boiling Test - 9.5%
  - Saturation Coefficient (C/B) - 0.66

- Production
  - 360 ton/day

- Fuel Consumption
  - 1000 BTU/pound fired ware
    6.3×10^6 BTU/1000 brick units

Brick Plant J

- Chemical Analysis

ANALYSIS	PERCENT
SiO_2	58.1
Al_2O_3	15.9
Fe_2O_3	6.3
K_2O	3.4
CaO	4.5
MgO	2.8
Na_2O	1.2

- Physical Properties Data

Compression strength	- 13,926 PSI
24-cold adsorption	- 6.0
5-hour boiling tests	- 7.9
Saturation coefficient C/B	- 0.75

- Production
  - 248 ton/day

- Fuel Consumption
  - 911 BTU/lb

Number/
Numéro

2

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS

PROGRESS REPORT
PHASE A – MILESTONE I

DSS FILE NUMBER	26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER	OSQ83-00230
CANMET PROJECT NUMBER	410252

POLLUTECH LIMITED 1090 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1900

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS
PHASE II

Progress Report

Phase A - Milestone 1

By

POLLUTECH LIMITED

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS FILE NUMBER : 26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER : OSQ83-00230
CANMET PROJECT NUMBER : 410252
CANMET SCIENTIFIC AUTHORITY : Mr. K. Bell

17pp

June 7, 1984

MICROMEDIA
OCT 11 1985

POLLUTECH LIMITED 1050 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1800

TABLE OF CONTENTS

Page No.

1. INTRODUCTION 1

2. ANALYTICAL PROCEDURES 2
   - 2.1 Sampling 2
   - 2.2 Sampling Preparation 3
   - 2.3 Pyrohydrolysis Procedure 4
   - 2.4 Fluoride Analysis 5
   - 2.5 Qaulity Control 6

3. TEST RESULTS 8

4. CONCLUSIONS AND RECOMMENDATIONS 10

TABLES

FIGURES

APPENDIX 1: Description of Samples Collected From the Brick Manufacturers

1. INTRODUCTION

This report summarizes the laboratory test results of Phase A - Milestone 1 of the CANMET project which is being carried out to examine means of inhibiting fluoride emissions from tunnel kilns for brickmaking by employing procedures alternate to conventional emissions control scrubbers. In particular, Phase A - Milestone 1 refers to the attainment and analysis of 30 samples from Canadian brick plants of major raw material, clay, shale or blend. Duplicate samples were analysed for fluoride content from each selected manufacturer.

An initial contact was made with each manufacturer by Pollutech staff in conjunction with technical support staff from the Ontario Research Foundation. Thereafter, Pollutech and ORF staff met with the Scientific Authority, Mr. Ken Bell, to choose the plants from which samples were selected for analyses. A listing of all the plants contacted, the raw materials urilized and site visits conducted is given in Appendix 1 of this report.

Analysis of the raw material was conducted using the currently accepted procedure of pyrohydrolysis of the sample followed by ion-selective electrode measurement of the resultant pyrohydrolysis liquor. Sampling procedures, preparation, pyrohydrolysis and analysis are detailed in Section 2 of this report.

2. ANALYTICAL PROCEDURES

In total some 63 samples of raw material were collected from 21 brick manufacturing plants across Canada. Although we were able to control the preparation and actual analysis for fluoride, we were not able to rigidly control the sampling procedures. An outline of our requested sampling procedure and analytical protocol follows.

2.1 Sampling

Of the 30 samples selected for analyses 3 were collected by Pollutech staff. The remainder were collected by the manufacturers, based on direction provided by Pollutech staff. We requested that the sample be collected to truly represent the actual raw product. Where several raw materials were blended, in several fashions, we requested samples of the individual raw materials.

The samples utilized for the fluoride analysis were selected by the Scientific Authority during discussions with Pollutech staff and Ontario Research staff. The samples were selected to adequately represent the variety of raw materials in use across Canada, and to provide coverage of all areas of Canada where brickmaking utilizing tunnel kiln technology was actively taking place.

The following samples from Canadian brickmaking plants were subjected to fluoride analysis:

- Brampton Brick, Brampton (Ontario)
- Toronto Brick, Toronto (Ontario)
- Domtar Brick,
    - Mississauga (Ontario)
    - Ottawa (Ontario)

- IXL - North West Brick & Tile, Edmonton (Alberta)
- IXL - Redcliff Press Brick, (Alberta)
- IXL = Medicine Hat Brick & Tile, Medicine Hat (Alberta)
- IXL - Medicine Hat Sewer Pipe, Medicine Hat (Alberta)
- IXL - Red River Brick & Tile, Winnipeg (Manitoba)
- IXL - Western Clay, Regina (Saskatchewan)
- Canada Brick, Streetsville (Ontario)
- Canada Brick , Burlington (Ontario)
- Citadel Brick Ltd., Ste. Anne (Quebec)
- Clayburn Industries Ltd., Abbotsford (British Columbia)
- L.E. Shaw Ltd., Halifax (Nova Scotia)
- Estevan Brick, Estevan (Saskatchewan)
- St. Lawrence Brick Co. Ltd., La Prairie (Quebec)
- Trinity Brick Products, St. John's (Newfoundland)

2.2 Sampling Preparation

All samples, upon arrival at Pollutech's Oakville laboratory, were tagged for future identification. A code number was assigned for identification of the sample and a separate laboratory code was assigned to ensure confidentiality of all data. All sample results reported herein are by laboratory code only, which is independent of the source of the raw material.

The raw material samples were dried at 45°C to remove excess moisture and promote particle separation. Larger clay materials were reduced in size using a mechanical grinder. The subsequent bulk powdere samples were split using a chute riffler. This was then followed by a more precise rotary riffling to supply a small representative sample for the pyrohydrolysis stage. Typically, a 10 gram sample was prepared by the riffling procedure.

The riffled sample was further ground to 200 mesh (ASTM) or less using an Agate Mortar (fluoride free). A 100 mg sample containing 0.1 to 4 mg of fluoride was weighed out. Approximately 250 mg of the catalyst (Vanadium pentoxide) was also weighed out. The 100 mg sample was ground with one-third of the vanadium pentoxide in the agate mortar, and this was then transferred to a quartz combustion boat. The remainder of the sample was extracted from the mortar by grinding with the Vanadium Pentoxide in two portions.

2.3 Pyrohydrolysis Procedure

The pyrohydrolysis apparatus, as depicted schematically in Figure 1, consists of the following major components:

- quartz tube furnace
- steam generator
- air supply
- condensor tube
- sample collector

To start the procedure the condenser is connected to the tube furnace exhaust for the collection of the steam condensate. A polyethylene bottle containing 5 ml of the alkaline absorbent solution is placed at the end of the condenser, with the end of the tube submerged. The quartz tube furnace is then preheated to 400°C.

The quartz combustion boat and sample, as previously prepared in accordance with Section 2.2, is placed at the mid point of the tube furnace. The temperature at this point had previously been checked by a rod thermocouple. The steam generator is now started and the tube furnace temperature is increased to 850°C. The system is maintained in this state until 200 mls of condensate have been collected. On average this step takes 100 minutes.

After collection of the first 200 mls of condensate, the air supply is turned on to collect the few final drops of condensate. The steam generator is then disconnected, and the sample boat is removed. At this point the furnace is turned down to 400°C and the steam generator is reconnected with the clean air purge. This cleaning process continues until the temperature has dropped to 400°C, a period of approximately 30 minutes.

The collected condensate is diluted to 250 mls for fluoride analysis by the ion selective electrode procedure.

Duplicate pyrohydrolysis runs were made on each sample of raw material.

2.4 Fluoride Analysis

The concentration of fluoride in the 250 ml condensate sample was determined by standard procedures utilizing an ion-selective electrode.

Initially the electrode was calibrated against a standard reference solution, prepared by serial dilution to 0.1 mg/L, 1.0 mg/L and 10 mg/L. An equal part of ISA/pH buffer was added to each standard. When the electrode was placed in the mid-range solution of 1.0 mg/L the meter was calibrated after 3 minutes of stirring. Following this the electrode was placed in the 10 mg/L standard, and after 3 minutes of stirring the temperature compensation was adjusted to give a full-scale reading. The meter is now set to read 0.1 mg/L to 10 mg/L directly.

Each condensate sample was treated with an equal part of the ISA/pH buffer, and thereafter the mg/L fluoride was determined by direct readout from the meter. This value was then used to determine the fluoride content on a weight ppm basis (mg/Kg) as follows:

$$\text{mg/L fluoride} \times \frac{250 \text{ ml sample}}{1000 \text{ ml}} \times \frac{1{,}000{,}000 \text{ mg/Kg}}{100 \text{ mg sample}} = \text{mg/Kg Fl}^{-}\text{(ppm)}$$

2.5 Quality Control

Several steps were taken by Pollutech's analytical staff to ensure that the fluoride results were accurate. Quality control procedures were utilized throughout the pyrohydrolysis/analysis stage as follows:

- duplicate tests were run on all samples including both the pyrohydrolysis and ion selective electrode analysis
- two (2) known standards were subjected to the test procedure, on multiple occasions, and all results were within plus or minus 5%
    - NBS standard #91 : Opal Glass
    - NBS standard #1206 : Phosphate Rock
- know weights of sodium fluoride (N_aF) were run through the pyrohydrolysis procedure, and additional known concentrations of N_aF were used to verify the ion-selective electrode procedure
- combustion boats were run through the pyrohydrolysis procedure empty and showed no fluoride

- combustion boats were re-fired in the pyrohydrolysis system after the preliminary test and no fluoride residual was detected

- two operators ran duplicate samples and achieved identical results on numerous occasions

In general we found the pyrohydrolysis plus ion-selective electrode procedure to be very stable. Any variation in fluoride content between these results and those reported elsewhwere would be more likely dependent on sample collection or other methods of fluoride analysis.

3. TEST RESULTS

As previously indicated, the raw material samples were coded to protect the confidentiality of the specific brick manufacturers. The code for the identification of the individual samples is known only by the Scientific Authority and senior Pollutech staff. The reporting of individual results to the manufacturers will be through the office of the Scientific Authority only.

The lab test results are given in the attached Table 1, which shows the result for both pyrohydrolysis runs and the corresponding average fluoride content of the material analysed.

The average fluoride content of the raw brick making material across Canada was found to be 706 ppm, with a peak level of 1163 ppm and a minimum level of 202 ppm.

On a percent-of-occurrence basis the following summary table outlines the range of levels found for fluoride in the raw material:

TABLE 2: FLUORIDE CONTENT OF RAW MATERIAL

Fluoride Levels ppm	Percent of Samples in Range
0-200	0
201-400	10.0
401-600	20.0
601-800	36.6
801-1000	20.0
1001-1200	13.4
1201-1400	0

In our analysis of the data we cannot refer to any "specific" trends in fluoride content of the raw material on a provincial area basis, as this would definitely result in the availability of confidential data on a plant specific basis. We have however observed a definite trend in the data on an "area" basis.

4. CONCLUSIONS AND RECOMMENDATIONS

Analysis of 30 samples of raw material utilized in the manufacture of clay-bricks using tunnel kiln technology shows a wide range in results. The fluoride content ranged from a low of 202 ppm to a high of 1163 ppm, with an average of 708 ppm. The presence of high levels of fluoride (i.e. greater than 900 ppm) in the raw material was prominent in specific areas of the country.

Sufficient data has now been collected to deliniate the presence of fluoride, and thus in conjunction with known production levels should allow for a selection of the 10 specific samples for the Phase A - Milestone 2 tasks. We would therefore recommend proceeding with Phase A -Milestone 2 and the corresponding selection of 10 samples for detailed examination in consultation with the Scientific Authority.

TABLE

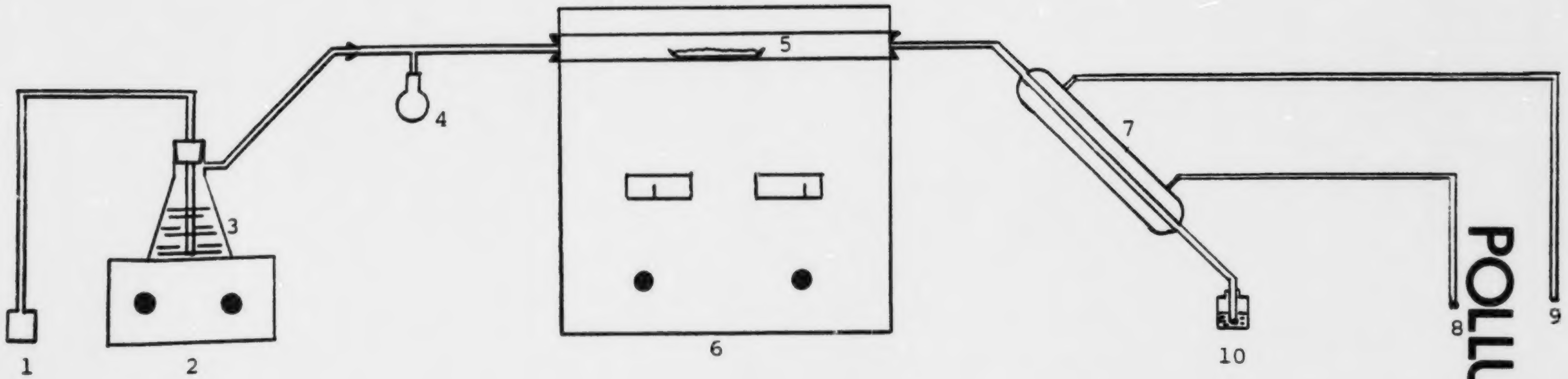
TABLE 1: RESULTS OF FLUORIDE ANALYSIS ON SELECTED RAW MATERIALS

Sample Code	Flourine Content (mg/kg) Test 1	Test 2	Average
2	750	800	775
3	700	688	694
11	950	1025	988
12	1125	1025	1075
15	500	520	510
17	205	198	202
18	650	600	625
19	1050	925	988
21	500	450	475
22	1075	1050	1063
26	725	725	725
27	1000	1025	1013
33	675	725	700
36	700	725	713
37	725	725	725
43	425	425	425
46	388	383	386
48	850	925	888
51	1175	1150	1163
56	400	425	413
59	438	423	431
61	925	925	925
67	450	475	463
68	613	650	632
70	900	913	907
76	263	250	257
82	700	700	700
83	725	700	713
86	975	1000	988
96	623	603	613
AVERAGE	706	705	706
MAXIMUM	1175	1150	1163
MINIMUM	205	198	202

FIGURE

FIGURE 1: PYROHYDROLYSIS UNIT

1. Air pump
2. Heater/stirrer unit
3. Fluoride free steam generator
4. Condensate trap
5. Sample boat
6. Tube furnace
7. Condensor
8. Cooling water input
9. To drain
10. Caustic sample trap



APPENDIX 1

DESCRIPTION OF SAMPLES COLLECTED FROM THE BRICK MANUFACTURERS

APPENDIX 1: Description of Samples Collected from the Brick Manufacturers

CODE NUMBER	PLANT	DATE COLLECTED	DESCRIPTION OF SAMPLE
TB-2703-1	Toronto Brick	March 27	Clean Shale Bank #1
TB-2703-2	Toronto Brick	March 27	Dirty Shale Bank #2
TB-2703-3	Toronto Brick	March 27	Sand Lime Brick
TB-2703-4	Toronto Brick	March 27	Extruded/Fired Shale #2,3,4 Sprayed
TB-2703-5	Toronto Brick	March 27	Extruded/Dried Shale #2,3,4 Unfired
TB-2703-6	Toronto Brick	March 27	Extruded Wet #2,3,4
BB-0204-7	Brampton Brick	April 2	Extruded Fired Brick
BB-0204-8	Brampton Brick	April 2	Extruded Undried Brick
BB-0204-9	Brampton Brick	April 2	Ground Shale Mesh 9
BB-0204-10	Brampton Brick	April 2	Blue Shale
BB-0204-11	Brampton Brick	April 2	Red Shale
HB-0504-12	Hamilton Brick	April 5	Crushed Raw and Scrap Brick
HB-0504-13	Hamilton Brick	April 5	Crushed Raw Aldershot
HB-0504-14	Hamilton Brick	April 5	Extuded/Undried HB-0504-12
HB-0504-15	Hamilton Brick	April 5	Extruded/Fired HB 0504-12
DC-0604-16	Domtar	April 6	Crushed Shale Both Pans-Mississauga
CB-0604-17	Canada Brick	April 6	Crushed Sand Shale-Burlington
CB-0604-18	Canada Brick	April 6	Crushed Copper Shale-Burlington
CB-0604-19	Canada Brick	April 6	Crushed Shale-Britannia Rd
CB-0604-20	Canada Brick	April 6	Crushed Shale-McFarren Plant
SL-1604-21	St. Lawrence	April 16	Laurentian Shale-La Prairie
IN-1804-22	IXL	April 18	Ground Local Red-Northwest
IN-1804-23	IXL	April 18	Local Sand-Northwest
IN-1804-24	IXL	April 18	Ground Athabaska Clay-Northwest
IR-1804-25	IXL	April 18	Ground 7 Mix-Redcliff
IR-1804-26	IXL	April 18	45 FR Sand-Redcliff
IR-1804-27	IXL	April 18	Ground 45 ABC-Redcliff
IR-1804-28	IXL	April 18	Ground 45D-Redcliff
IM-1804-29	IXL	April 18	Ground Rav.A2-Medicine Hat
IM-1804-30	IXL	April 18	Ground Rav.E-Medicine Hat
IM-1804-31	IXL	April 18	Ground 34L-Medicine Hat
IM-1804-32	IXL	April 18	Ground 66.2 Medicine Hat
IM-1804-33	IXL	April 18	Ground 39 Clay Medicine Hat
IM-1804-34	IXL	April 18	Ground Q9-Medicine Hat
IM-1804-35	IXL	April 18	Ground Rav. B.D.-Medicine Hat
IM-1804-36	IXL	April 18	Ground PP.BCD-Medicine Hat
IM-1804-37	IXL	April 18	Ground 45R-Medicine Hat
IM-1804-38	IXL	April 18	Ground 82C-Medicine Hat
IM-1804-39	IXL	April 18	Grund 81 Buff Medicine Hat
IM-1804-40	IXL	April 18	Ground 34 Mix Medicine Hat
IM-1804-41	IXL	April 18	Ground 34F Medicine Hat
IR-1804-42	IXL	April 18	Ground Morden Shale-Red River
IR-1804-43	IXL	April 18	Ground Manitou Shale-Red River
IR-1804-44	IXL	April 18	Ground St. Rose K Clay-Red River
IR-1804-45	IXL	April 18	Ground HIR Clay-Red River
IR-1804-46	IXL	April 18	317 Sand-Red River
IR-1804-47	IXL	April 18	Ground Stoneware Clay-Red River
IR-1804-48	IXL	April 18	Ground Broken Head Clay-Red River
IW-1804-49	IXL	April 18	Ground Av.W.P.-Regina
IW-1804-50	IXL	Aril 18	Ground Adams Clay-Regina
DO-2304-51	Domtar	April 19	Ground Shale-Ottwa
CB-2304-52	Citadel Brick	April 23	Crushed American Shale-St. Anne
CB-2304-53	Citadel Brick	April 23	Ground St. Appollinaire Shale-St. Anne
CB-2304-54	Citadel Brick	April 23	Ground Beauport Shale-St. Anne
DQ-2504-55	Domtar	April 23	Ground Shale-La Praire
CI-1005-56	Clayburn Ind.	May 4	Crushed Red Shale-Abbotsford
CI-1005-57	Clayburn Ind.	May 4	Crushed Straiton Buff-Abbotsford
CI-1005-58	Clayburn Ind.	May 4	#9 Clay-Abbottsford
CI-1005-59	Clayburn Ind.	May 4	Diatomite-Abbottsford
LS-1010-60	L.E.Shaw	May 10	Lantz Glasgo Shale-Halifax
LS-1105-61	L.E.Shaw	May 11	Lantz Shubie Clay-Halifax
LS-1105-62	L.E.Shaw	May 11	Lantz Milford Shale-Halifax
LS-1105-63	L.E.Shaw	May 11	Lantz Red Clay-Halifax
EB-1105-64	Estevan Brick	May 11	Rockglen Shale
EB-1105-65	Estevan Brick	May 11	Willows Plastic Shale
EB-1105-66	Estevan Brick	May 11	Flintoft Plastic Shale
EB-1105-67	Estevan Brick	May 11	Lalonde Shale
BS-3105-68	Brique Scott	May 31	#1 Clay
BS-3105-69	Brique Scott	May 31	#2 Shale
BS-3105-70	Brique Scott	May 31	#3 Clay
LS-0406-71	L.E.Shaw	June 4	Ground Clay-Chipman
TB-2007-72	Trinity Bricks	July 20	Precambrian Shield-St. John's

Number/
Numéro

3

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS

PROGRESS REPORT
PHASE A – MILESTONE 2

DSS FILE NUMBER	26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER	0SQ83-00230
CANMET PROJECT NUMBER	410252

69 pp

MICROMEDIA
OCT 11 1985

POLLUTECH LIMITED 1090 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1900

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS
PHASE II

Progress Report

Phase A - Milestone 2

By

POLLUTECH LIMITED

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS FILE NUMBER : 26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER : OSQ83-00230
CANMET PROJECT NUMBER : 410252
CANMET SCIENTIFIC AUTHORITY : Mr. K. Bell

March 31, 1985

POLLUTECH LIMITED 1090 SPEERS ROAD OAKVILLE ONT L6L 2X4
TELEPHONE (416) 844-1900

TABLE OF CONTENTS

Page No.

1. INTRODUCTION 1

2. SUB-CONTRACT REPORT FROM THE ONTARIO RESEARCH FOUNDATION 2

APPENDIX A - Sub-Contractors Report

1. INTRODUCTION

As part of the work outline for Phase A - Milestone 2 of this study, Pollutech Limited arranged for a Canadian researcher competent in brickmaking technology and the thermochemistry of silicates, to attend at the fluoride evolution testing in Germany. Pollutech Limited subcontracted this portion of the project to the Ontario Research Foundation, and in particular to Dr. Ivan Joyce, Manager of ORF's Mineral Reources Centres.

Dried green brick samples from ten Canadian brickmaking plants were air freighted to the Institute Für Zigelforschung in Essen, West Germany for the detailed testing. The work at the German Research Centre was co-ordinated through Dr. Hauck.

Direction as to sample testing procedures (i.e. firing profiles) were provided by Pollutech Limited, based upon the actual kiln profile data collected during the site visits. Detailed technical reports on each plant were taken to Germany by Dr. Joyce for further discussions with Dr. Hauck on Canadian brickmaking technology. Copies of the reports on the Canadian facilities were submitted previously to CANMET, and are also summarized in the Phase A Final Report.

2. SUB-CONTRACT REPORT FROM THE ONTARIO RESEARCH FOUNDATION

A complete technical report outlining the purpose of the tests at the Institute Für Zigelforschung, the details of the testing procedures, and the test results, has been prepared by the Ontario Research Foundation. A complete copy of the technical report is included as Appendix A of this Phase A - Milestone 2 report.

Included in the attached technical report are copies of the original German test results from the Institute Für Zigelforschung. Technical translations have been made of these reports that, are to the best of our knowledge, accurate representations of the German findings.

APPENDIX A

TECHNICAL REPORT PREPARED BY
THE ONTARIO RESEARCH FOUNDATION

MATERIALS DIVISION
Mineral Resources Centres

THE DETERMINATION OF FLUORINE EMISSION PROFILES FOR CLAY-BRICK RAW MATERIALS

Report on visit to Institut fur
Ziegelforschung, Essen E.V.
to observe and discuss techniques

prepared for

Pollutech Limited
1090 Speers Road
Oakville, Ontario
L6L 2X4

Attention: Mr. R. V. Laughton

RESEARCH

SHERIDAN PARK RESEARCH COMMUNITY
MISSISSAUGA, ONTARIO, CANADA L5K 1B3 • (416) 822-4111 • TELEX 06 982311

THE ONTARIO RESEARCH FOUNDATION [illegible]
4. NO REPORT ISSUED BY US SHALL BE PUBLISHED IN WHOLE [illegible] CONSENT
5. OUR NAME SHALL NOT BE USED IN ANY WAY IN CONNECTION [illegible] OF ANY ARTICLE, PROCESS OR SERVICE
6. WE RESERVE THE RIGHT NOT TO COMMENCE AND/OR CONTINUE [illegible] ARRANGEMENTS SATISFACTORY TO US ARE ESTABLISHED

CONTENTS

Page

FOREWORD 1

1. INTRODUCTION 2

2. SAMPLE COLLECTION PREPARATION AND SHIPMENT 3

3. ANALYTICAL EQUIPMENT/PROCEDURES 4

4. EXPERIMENTAL WORK AND RESULTS 6

5. DISCUSSION AND COMMENTARY 7
   - 5.1 The Analytical Technique for Measurement of Fluoride Emission Profiles 7
   - 5.2 Fluoride Emission Profile Data Generated 8
   - 5.3 General Aspects of Fluoride Emissions and their Suppression 10

6. CONCLUSIONS 11

REFERENCES 12

FOREWORD

Ontario Research Foundation was subcontracted by Pollutech Limited to provide technical expertise for their DSS/CANMET sponsored program (DSS Contract No. 0SQ83-00230) on "The Effect of Fluoride Control Systems on the Energy Efficiency of Tunnel Kilns Manufacturing Structural Clay Products - Phase II". As part of this subcontract, ORF staff were required to visit the Institut fur Ziegelforschung, Essen E.V., and the Institut fur Silicatforschung in Wurtzburg to both observe and discuss the technique for the measurement of fluoride emission profiles being employed on Canadian clay brick samples at the Essen facility. It was considered necessary to determine whether the technique was of value to the industry and whether it could be readily transferred to a Canadian laboratory. In addition, discussions were held with experts at the two institutions to determine what steps might be taken to minimize or eliminate fluoride emissions from clay brick plants.

It was a requirement of the contract issued by DSS/CANMET that this separate report be issued, recording the visit and the technical information obtained.

1. INTRODUCTION

Since the evolution of fluoride from clays and shales is a temperature sensitive reaction, and because the rate of fluoride evolution increases as the operating temperature approaches the vitrification range, it is considered that modification of the firing schedule in clay brick kilns could have a significant effect upon the fluoride emissions from clay brick manufacturing plants.

Recent laboratory studies in Germany by Tunker and Schmidt(1) and Kother & Pauls(2) on emission rates for fluoride evolution from clays have indicated that modification and control of the kiln temperature profile and/or a simple reduction in the final firing temperature will provide a means of reducing and/or controlling fluoride emissions from ceramic plants.

Their studies have shown that the rate of the fluoride emission is not constant with temperature rise. It is dependent upon a number of variables, the most important of which is the concentration of water vapour in the kiln atmosphere. The emission of fluoride is also independent of the total fluoride content of the raw materials (i.e. all of the fluoride is not necessarily emitted during firing). While fluoride evolution commences in the range of 550°C to 750°C, the rate of evolution increases markedly at temperatures greater than 850°C and is generally completed before the final firing temperature is reached. The cessation of fluoride emission is considered to be due to the onset of vitrification, which seals up the body, thus preventing further diffusion of fluoride-bearing gases to the surface. It has also been noted that because the rate of fluoride evolution is particularly rapid above 850°C, it would be beneficial to heat the products from 850°C to the required final firing temperature as quickly as possible, thereby minimizing the period during which fluoride evolution can occur, and ensuring the rapid onset of vitrification to seal up the pore structure of the product.

Even though such an accelerated heating rate in the region of 850°C to the final firing temperature will result in a surge in fuel consumption, the total consumption per unit production for the entire firing cycle may be reduced due to faster kiln throughputs.

The work of Tunker and Schmidt, and Kother and Pauls in West Germany on fluoride emission profiles has been conducted at the Institute for Silicate Research in Wurtzburg, and the Institute fur Ziegelforschung in Essen, respectively, it is evident from their publications that measurements of fluoride emissions and the combined influence of water vapour concentration and temperature and their relationship to idealized firing schedules are a routine function in those laboratories. As a consequence, it was considered preferable to submit typical Canadian brick samples for analysis in one of the West German facilities, and to send an observer to provide aid and learn the details of the analytical technique. The Institut fur Ziegelforschung in Essen was selected to conduct the analysis because of their familiarity with brick manufacturing techniques and rapid turnaround time.

2. SAMPLE COLLECTION PREPARATION AND SHIPMENT

Representative green brick samples, together with physical property data and typical firing schedules, were collected from ten (10) different clay brick manufacturing plants during familiarization field visits. The ten brick plants were selected in conjunction with the Scientific Authority, and represented typical raw materials and brick manufacturing practices across Canada. Samples were collected from Nova Scotia, Quebec, Ontario, Manitoba and Alberta, and represented a wide range of brick-making clays and shales. Upon receipt of the samples by Pollutech Limited, they were number-coded to preserve confidentiality in reporting. The code numbers used to identify the samples were 100, 102, 103, 104, 105, 107, 108, 109, 110 and 111.

A minimum of eight (8) samples were collected from each plant, and depending upon production conditions and schedules, some were received in the wet green state; these were subsequently dried carefully at Ontario Research to provide "mechanically sound" samples for air shipment to West Germany. Quadruplicate (mechanically sound) samples were selected from each set, sealed and wrapped in plastic, and then tightly packed in polystyrene and crated. The packaged samples were then shipped by air freight to the Institut fur Ziegelforschung in Essen, West Germany, for measurement of Fluorine Emission Profiles.

All of the samples arrived intact at the Institut fur Ziegelforschung.

3. ANALYTICAL EQUIPMENT/PROCEDURES

The equipment used at the Institut fur Ziegelforschung to determine the fluorine emission profile of clay products was not specifically designed for this procedure, but basically consisted of a muffle furnace which has been modified to permit controlled air and moisture flow over the ware. The furnace possessed a gas exit port, through which the furnace atmosphere and the gaseous products of thermal decomposition could pass, which, in turn, was coupled to a gas sampler and collector which also contained a fluoride detection system.

The furnace (see Figure 1) used an 'Inconel 6001' refractory metal muffle which was closed at one end (with the exception that it possessed a narrow exit port (~2 cm diameter) to allow flow through of furnace gases). The overall dimensions of the furnace were approximately 2.5 metres long by 1.5 metres wide and 2 metres in height. The dimensions of the muffle chamber were 2.5 metres long by 0.3 metres wide by 0.25 metres high. The furnace was powered by electricity and utilized 3 separately controlled wire windings to provide accurate temperature control in the central firing zone. The furnace controllers utilized metal 'cams' cut to the desired heating profiles.

The brick samples to be tested were placed in the centre of the furnace sitting on their back, or face, with the cores parallel to the direction of air flow through the kiln. Excess volume on either side of the brick was filled with hollow, sealed Inconel boxes to reduce the volume of 'dead' air within the furnace. Once the heating cycle had been initiated, air was pumped into the furnace at a rate of 880 litres of air/hr. (or 0.88 cubic metres of air/hr.), and moisture was introduced into the furnace at the desired level by injection of water just inside the door from a metering peristaltic pump. The air and water lines to the furnace were insulated and the furnace door was heated by an oil jacket to prevent condensation of water on the inner surface of the door.

A representative portion of the gas stream leaving through the exit port of the furnace was sampled, filtered and delivered to a commercial Bran and Lubbe Sensimeter G (see Figure 2) capable of continuously monitoring fluoride by a specific ion electrode technique. The key to the sampling and measurement system was a combination of pump and valve interlocks which removed exhaust gas from the gas stream at a controlled rate of 40 litres/hr, and bubbled it through an automatically measured volume (5.25 ml) of sodium acetate/E.D.T.A. buffer solution over a period of 6 minutes. After this time it discharged the resulting solution to a specific ion electrode cell to monitor the fluoride concentration and compare it against a standard solution. This process was repeated automatically every 6 minutes throughout the firing; the specific ion electrode cell was flushed with distilled water automatically between each reading. The signal from the specific ion electrode cell was logged in a computer connected to the apparatus and when the run was complete, cumulative fluoride emission and emission rates versus temperature were plotted.

The specific ion electrode cell was maintained at $40^{o}C \pm 0.1^{o}C$ during the course of the analysis.

The buffer solution used for the analysis was made up as follows.

800 ml of distilled water
41.0 g of sodium acetate - ($CH_3COONa.3H_2O$)
0.4 g of Titriplex III - E.D.T.A., disodium salt
3.0 ml of acetic acid - 96%

The whole was then made up to a volume of one litre.

Schematics of the exhaust gas stream sampler and the 'internals' of the Bran and Lubbe Sensimeter G fluoride analyser are shown in Figures 3 and 4, respectively.

It is considered that the 'Sensimeter G' system is not totally automatic, it does require some attention and another technique to calibrate the system together with a knowledge of the gas chemistry to provide meaningful results.

A schematic of the combined furnace assembly as observed is shown in Figure 5.

Technical brochures outlining the features of the Bran and Lubbe Sensimeter G, together with a cost quotation, are attached in Appendix 2.

4. EXPERIMENTAL WORK AND RESULTS

Fluorine Emission Profiles were determined for all of the Canadian samples supplied to the Institut fur Ziegelforschung in the apparatus described. Firing profiles used for each sample run were as provided by the respective plants. In addition, fluoride analysis of both the green and fired samples was also determined. The results obtained were reported to ORF in Test Report No. K2706. The report was prepared in German and was translated into English by ORF staff. The test report together with the English translation are included in their entirety in Appendix 1.

Briefly, it was noted in the report that the Canadian raw materials exhibited high natural fluoride contents compared to the European experience, and all of the fluorine emission profiles were different. The high fluoride contents, however, do not necessarily mean that all materials exhibit high fluoride emissions. In many cases approximately 50% of the fluoride was reportedly evolved, but in one case (sample 104) only 15% was emitted during the recommended firing schedule.

Fluoride emissions generally begin between 700°C and 750°C, although samples 104, 107 and 111 initiate their fluorine emissions at higher temperatures (around 800°C or higher). Also in most cases, the brick samples reached their maximum emission rate prior to reaching the peak firing temperature.

Three methods of approach were suggested for the reduction of fluoride emissions:

(i) the incorporation of a flux to lower the firing temperature,
(ii) the experimental use of limestone additions to capture the fluoride in the form of calcium fluoride CaF_2,
(iii) the application of different firing procedures, e.g. faster heating rates and lower peak temperatures.

5. DISCUSSION AND COMMENTARY

5.1 The analytical Technique for Measurement of Fluoride Emission Profiles

In principle, the analytical technique used at the Institut fur Ziegelforschung to measure fluorine emission profiles is relatively simple, the commercial automatic gas analysis unit provides the critical 24-hour monitoring step required for long firing schedules.

The furnace system, used to fire the products and generate the gaseous fluoride decomposition product, performs adequately but could be significantly improved upon. A more compact furnace which would be inexpensive and easier to access and clean could be made using a fused quartz tube and appropriate heating elements and insulation mounted in a vertical configuration. Such a system would be similar to that currently used(3) at the British Ceramic Research Association to monitor water and organic emission profiles from clay products (see Figure 6). Such a system would allow for the brick sample to be placed in the system vertically, and would significantly reduce the potential 'dead' space and improve the purging of the system (extraction of furnace gases).

The 'Sensimeter G' system for the measurement of fluoride ion appears to work very well in the system observed, however since the technique is based upon a continuous automatic specific ion electrode, it was reported by the German scientific staff that experienced technicians are required to ensure its smooth operation.

Since the fluoride analyzer is a commercial unit and since a suitable furnace could be easily custom made, this technology could be readily transferred to Canada if desired. Early reports from Germany that the furnace system needed to be specially constructed and lined with platinum appear to be unfounded.

5.2 Fluoride Emission Profile Data Generated

It would appear from the fluoride emission profiles generated that the curves can be used as a 'fingerprint' for the raw material under investigation in the same way that Differential Thermal Analysis (DTA) curves are used. However, it is believed that in this particular case, the curves are not only a function of the raw material, the firing profile and furnace atmosphere, but also to some extent they are a function of the furnace design. In the case of the Canadian samples under investigation, the moisture content of the furnace was controlled at 3%.

An evaluation of the actual fluoride emission rate data and comparison of these data with the total fluoride emitted and residual fluorine in the fired products clearly indicates that, generally speaking, all of the fluoride which is going to be evolved has in fact done so by the time that the brick sample reached its maximum temperature. Therefore, the curve maximum and tail are in fact not measurements of continuing emissions but measurements of 'washout', or fluoride retained within the furnace atmosphere (i.e. within 'dead' space and corners) which was not flushed out immediately after evolution from the sample. The shape of the curve maximum and 'tail' would depend upon the size of the exit port, the rate of flow of gases over the ware and the ease of purging of the furnace atmosphere. The presence of the Inconel boxes to reduce dead space in the German furnace may in fact have resulted in poor purging and washout characteristics for the gaseous fluoride evolved. Nevertheless, the information generated by the technique is extremely valuable and, as previously stated, can be used as an analytical tool (for any given design of furnace).

In interpreting the data, it is important to remember that the curves generated do not commence plotting until fluoride is first detected, consequently the scales on the axes of the graphs generated require care when comparing one with another. In particular, the time axis only relates to the time of actual fluorine emission, not the time of the firing cycle.

The data for the Canadian samples are extremely interesting. The curves are all significantly different, but they are not only different raw materials manufactured with a variety of different equipment, but they were also fired according to differing (production plant) schedules. It was not determined as part of this study whether changing the firing schedule (e.g. faster firing) for any given raw material would significantly change the fluoride emission profile and total fluoride evolved. However, it is interesting to note that in the case of sample #104, the combination of raw material and firing schedule resulted in a reported fluorine emission of only 15% of the total fluorine available. If the concept of using firing control to optimize (minimize) fluoride emissions is to be tested further, then two additional studies would appear to be warranted:

(i) maintaining all other conditions equal, determine the effect of variations in the firing schedule on fluoride emission profiles and total fluoride evolved;

(ii) determine the importance of mineralogical composition upon the fluoride emission profiles for given firing conditions.

5.3 General Aspects of Fluoride Emissions and their Suppression

General discussions with the scientific staff at the two West German research institutions indicated that they believed that the greatest gains to be made in the suppression of fluoride emissions by firing control was by reducing the top firing temperatures - by either producing a lower quality product or by the addition of fluxes to reduce the sintering temperature. (This approach is echoed in the report in Appendix 1.)

Due to a tightening of West German environmental regulations which come into force in 1985, the West German approach to control of fluoride emissions has moved more strongly towards:

(a) the use of additives to 'fix' the fluoride, and more importantly,

(b) dry scrubbing using granulated calcium carbonate and calcium hydroxide.

Work on additives to fix the fluoride and prevent it being evolved have principally centred around the use of calcium carbonate. It has been shown that ultra-fine natural calcium carbonate (possessing a high reactivity) can in fact fix fluoride and minimize its emission, however it would appear that the crystallinity, morphology and chemistry of the $CaCO_3$ are important to the effect as well as the size (minus 2 microns). It was reported that there were only two natural sources of suitable calcium carbonate in Germany which actually produce the desired effect. Furthermore, there appears to be an optimum level of addition for maximum effect. Apparently(4) fluorine emissions can be reduced by up to 50% for an optimum addition, after which emission levels rise with further additions of $CaCO_3$.

Work on dry scrubbing techniques has progressed to a very high level where scientific staff at the two institutions are now confident that if the new stricter regulations are enforced in Germany, then the brick industry will be able to respond. However, the solution will be very expensive. Current technology is based upon a scrubber consisting of a sequence of rotating trays containing pelletized absorbent ($CaCO_3$ and $Ca(OH)_2$). The flue gases are forced to pass through and over the trays several times before exhausting through a baghouse facility. Solid waste is then disposed of by landfilling.

6. CONCLUSIONS

(1) Fluorine emission profiles conducted on ceramic raw materials can be a very useful tool to ascertain the characteristics of fluorine evolution from ceramic plants. The profiles produced are dependent upon furnace design, firing schedule and raw material chemistry (geology).

(2) The technique for measuring fluorine emission profiles is basically very simple, employing custom made (modified) furnaces in which temperature and furnace atmosphere can be readily controlled to typical industrial situations. The gas analysis instrumentation required is commercially available, thus the methodology can be readily transferred and adapted in Canada.

(3) In general, rates of fluoride emission for the Canadian raw materials are very high just prior to achieving maximum firing temperatures such that all of the fluoride which is going to be evolved has in fact done so before the top temperature is attained. Consequently, simple changes in firing rate alone just prior to achievement of the top temperature and/or minor reductions of the maximum temperature are not likely to make major improvements on the fluoride emission. It is more likely that a combination of changes in raw material chemistry and controlled shorter firing schedules will have a greater impact as shown by the results for sample #104.

(4) Since it was beyond the scope of this program to monitor the effects of raw material chemistry and varying firing schedules upon fluorine emission, it is considered that further studies are warranted to determine the mutual interaction of these parameters with a view to minimizing fluoride evolution.

I. H. Joyce
Manager
Mineral Resources Centres

E. C. Brown
Director
Materials Division

REFERENCES

1. G. Tunker and H. Schmidt, "Solution to a Fluorine Emission Problem in stoneware production", Ziegelindustrie 3, p. 173, 1983.

2. W. Kother and N. Pauls, "Determination of a Production Firing Curve for Optimum Fluorine Bonding in Brick Firing", Ziegelindustrie 3, p. 167, 1982.

3. R. W. Ford, "Some Aspects of Firing Carbonaceous Materials", Transactions and Journal of British Ceramic Society, Vol. 83(5),p. 126, 1984.

4. Institut fur Ziegelforschung - Private Communication.

Figure 1

Muffle Furnace Used for Measurement of Fluorine Emission Profiles at Institut fur Ziegelforschung, Essen E.V.

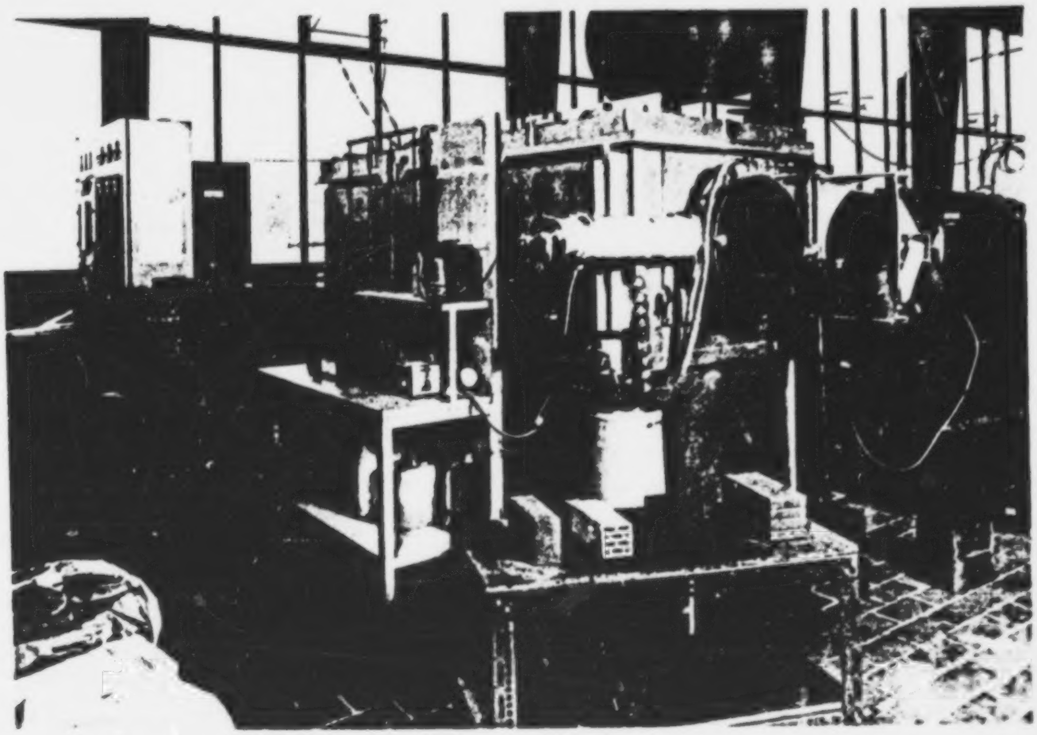
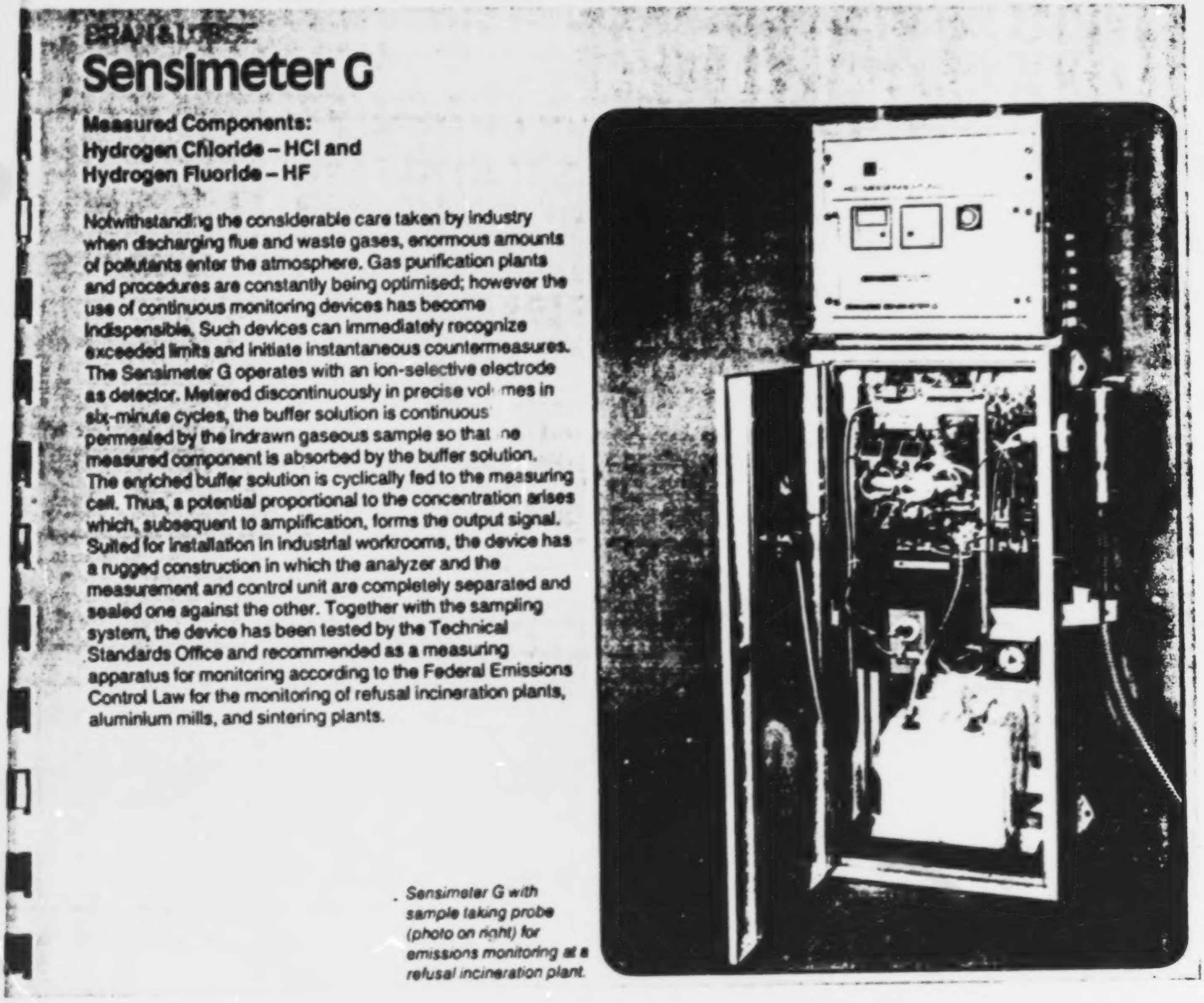


Figure 2



BRAN&LUEBBE

Sensimeter G

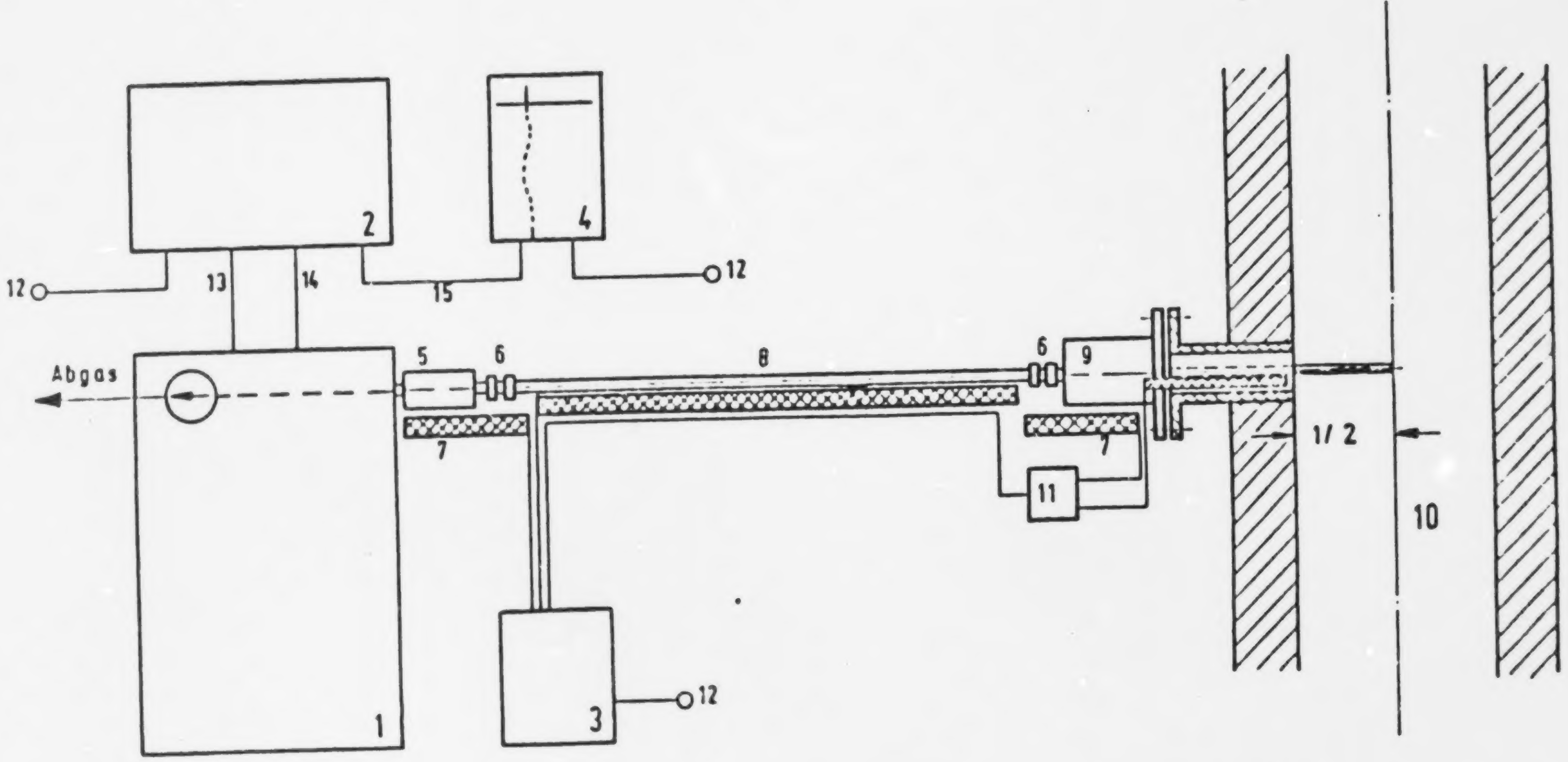
Measured Components:
Hydrogen Chloride – HCl and
Hydrogen Fluoride – HF

Notwithstanding the considerable care taken by industry when discharging flue and waste gases, enormous amounts of pollutants enter the atmosphere. Gas purification plants and procedures are constantly being optimised; however the use of continuous monitoring devices has become indispensible. Such devices can immediately recognize exceeded limits and initiate instantaneous countermeasures. The Sensimeter G operates with an ion-selective electrode as detector. Metered discontinuously in precise volumes in six-minute cycles, the buffer solution is continuously permeated by the indrawn gaseous sample so that the measured component is absorbed by the buffer solution. The enriched buffer solution is cyclically fed to the measuring cell. Thus, a potential proportional to the concentration arises which, subsequent to amplification, forms the output signal. Suited for installation in industrial workrooms, the device has a rugged construction in which the analyzer and the measurement and control unit are completely separated and sealed one against the other. Together with the sampling system, the device has been tested by the Technical Standards Office and recommended as a measuring apparatus for monitoring according to the Federal Emissions Control Law for the monitoring of refusal incineration plants, aluminium mills, and sintering plants.

Sensimeter G with sample taking probe (photo on right) for emissions monitoring at a refusal incineration plant.

Figure 3

Exhaust Gas Stream Sampler


2
4
12
13
14
15
12
12
Abgas
5
6
8
6
9
7
7
11
1/2
10
1
3
12

1 Analysator Sensimeter G
2 Steuerteil
3 Schaltschrank mit Temp. Regelung für Gasentnahmesystem
4 Registriergerät
5 Staubfilter
6 Rohrverbinder 10 mm Ø
7 Heizmanschette
8 Probenahmeleitung (flexibel-beheizt)
9 Entnahmesonde (beheizt) mit Staubfilter
10 Kamin
11 Klemmenkasten
12 Netzanschluß
13 Steuerleitung
14 Meßleitung
15 Meßsignal

Figure 4

Schematic of Sensimeter G

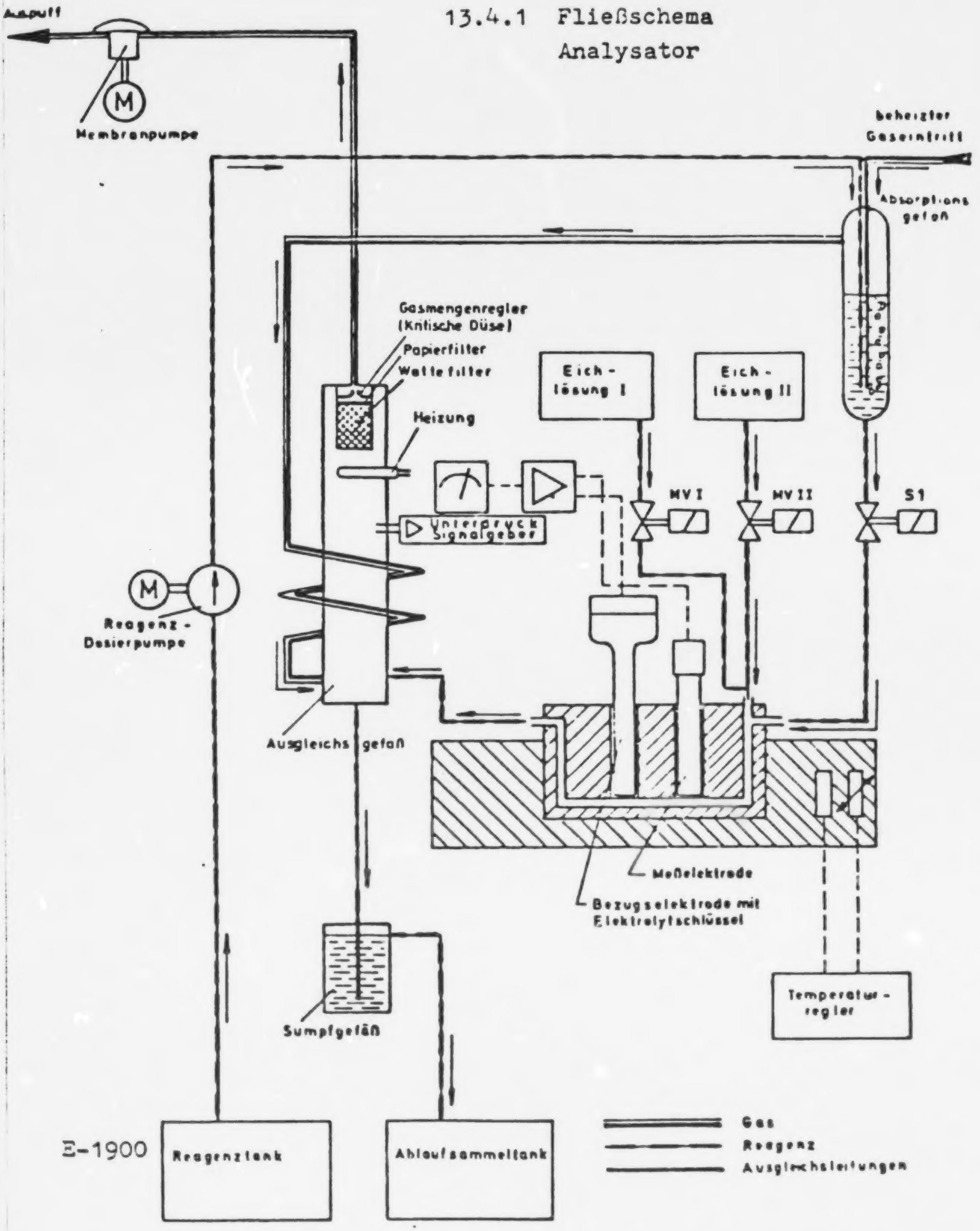

13.4.1 Fließschema
Analysator
Auspuff
M
Membranpumpe
beheizter
Gaseintritt
Absorptions
gefäß
Gasmengenregler
(kritische Düse)
Papierfilter
Wattefilter
Heizung
Eich-
lösung I
Eich-
lösung II
MV I
MV II
S1
Unterdruck
Signalgeber
M
Reagenz-
Dosierpumpe
Ausgleichsgefäß
Meßelektrode
Bezugselektrode mit
Elektrolytschlüssel
Sumpfgefäß
Temperatur-
regler
Reagenztank
Ablaufsammeltank
Gas
Reagenz
Ausgleichsleitungen

Figure 5

Schematic Diagram of Furnace and Fluoride Analyzer for Determination of Fluorine Emission Profiles

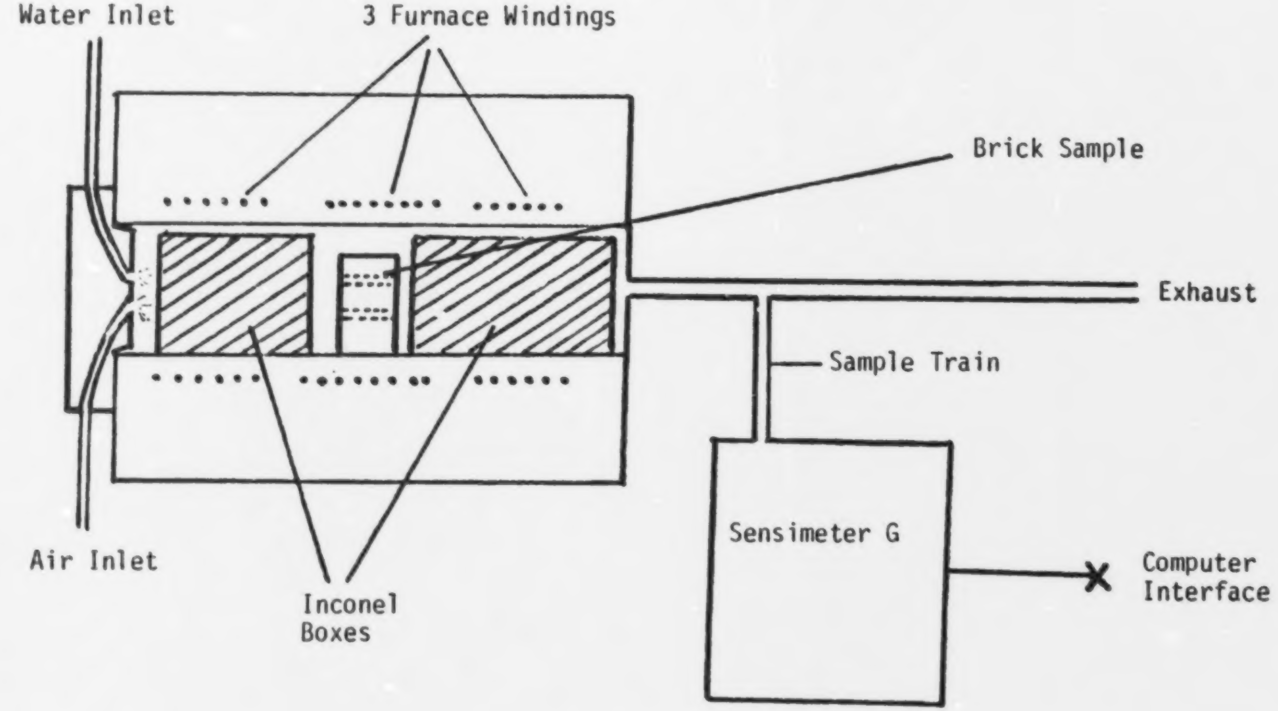
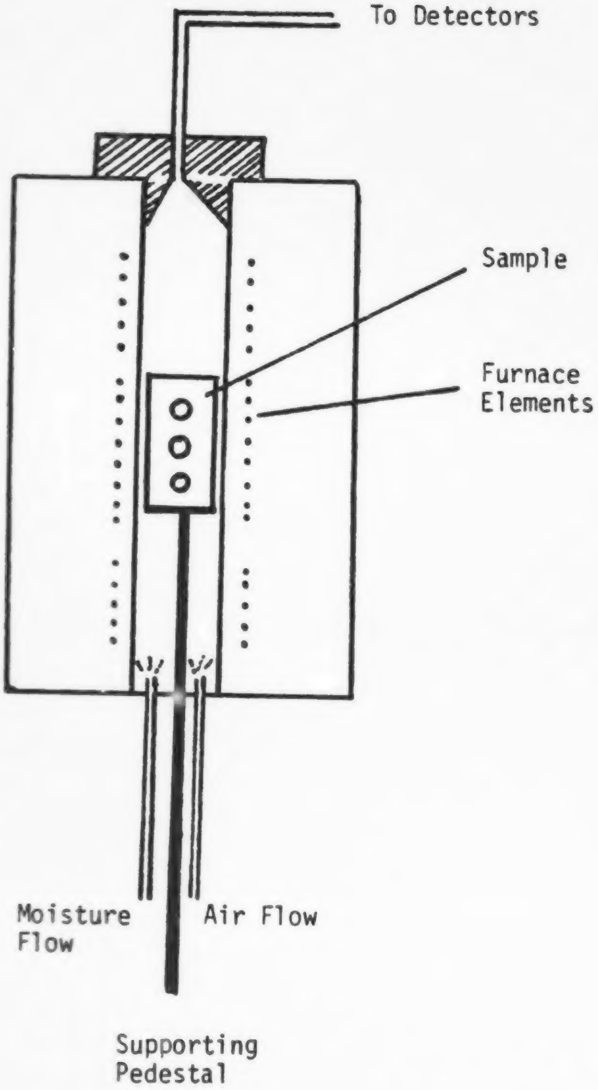

Water Inlet
3 Furnace Windings
Brick Sample
Exhaust
Sample Train
Air Inlet
Inconel Boxes
Sensimeter G
Computer Interface

Figure 6

Schematic Diagram of Vertical Tube Furnace Assembly Suitable for Determination of Fluoride Emission Profiles


To Detectors
Sample
Furnace Elements
Moisture Flow
Air Flow
Supporting Pedestal

APPENDIX 1

Report by the Institut fur Ziegelforschung on fluorine emission behaviour of Ten Canadian Clay Brick Samples

(a) English Translation
(b) Original German Text

Institut fur Ziegelforschung, Essen E.V.

Translation* of Test Report No. K2706

Sponsor:	ORF
Purpose of Request:	Determination of Fluorine-emission behaviour of original-brick using a special muffle-furnace
Diecut:	Same as sponsor
Receipt of Samples:	20 November 1984 and 12 February 1985 (Sample No. 111)
Samples Available:	Four green brick (each) = I 9004 No. 100, 102. 103, 104 105, 107, 108, 109, 110, 111

CONTENTS

1. INTRODUCTION

2. EXPERIMENTAL PROCEDURE CONCERNING FLUORINE-EMISSION BEHAVIOUR

3. FLUORINE DETERMINATION

4. RESULTS

---

* Translation prepared by Ontario Research Foundation

1. INTRODUCTION

The Institute for Brick Research has been asked to determine the fluorine-emission behaviour of 10 green brick samples using a special muffle-furnace and plant-heating curves submitted by the client. In addition, the fluorine concentration of raw and burnt brick samples has been determined by chemical analyses. It was a special requirement to establish in which temperature region of the heating zone fluorine-emission primarily takes place.

2. EXPERIMENTAL

In order to determine their fluorine-emission behaviour, the 10 green brick samples supplied by the client were heated in an oxidizing atmosphere using an electrically heated, airtight, special muffle furnace, and the 10 different plant-heating curves supplied by the client. Cooling was not controlled according to the firing schedule provided, but following a natural (furnace dependent) trend.

The moisture concentration of the furnace atmosphere was - as agreed with the client - for all firings using about 30 g/kg dry air, and maintained constant over the entire burn period.

The fluorine concentration in the exhaust gas and the firing temperature were recorded continuously during the burn. By means of a computer, and considering the flow-through of air as well as the various weight losses during the burn, these data have been used to calculate the following parameters:

(a) Fluorine-Emission Rate, given in mg fluorine/kg x hr. which shows how many mg/fluorine are emitted per kg product per hour at a specific temperature,

(b) Integrated Fluorine-Emission, with the units of mg Fluorine/kg of fired product, which shows how many mg Fluorine have been emitted per kg of fired product up to a specific temperature.

The parameters described under (a) and (b) have been plotted against firing time using a recorder connected to the computer. It should be pointed out that the curves show only the time between beginning and end of the fluorine emission (time of fluorine-emission). The results of the experimental burns with the brick samples are shown in Figs. 1-10.

3. FLUORINE DETERMINATION

The results of the chemical analyses obtained with green and fired brick samples are given in the Appendix (Test Report CH 3977).

4. EXPERIMENTAL RESULTS

Initially, it should be noted that the Institute for Brick Research was not in the possession of information which could be used to characterize the raw material such as chemical and x-ray diffraction analysis. In addition, the Institute did not have data on product properties, for example, water absorption and shard porosity of the burnt materials, which, as is well known, can have a considerable influence on fluorine-emission.

The results of the determination of the fluorine-emission rate obtained with the Institute's special muffle-furnace for the 10 original green brick samples supplied by the client are given in Figs. 1-10. These show, first of all, fluorine emission begins for most of the samples examined at a temperature of 700 - 750°C in the region of the heating zone, i.e. for samples 100, 102, 103, 104, 105, 108, 109 and 110. Only for samples 107 and 111 was the beginning of the fluorine emission at 800°C. In connection with this difference, it should be noted that certainly the beginning of the fluorine emission is among other factors, dependent upon the heating cycle experienced by the specific bricks prior to the beginning of the fluorine-emission.

At further examination of the curves for the fluorine-emission, it is noticeable that most of the brick samples reach the maximum of their fluorine emission prior to the beginning of the peak temperature, which is particularly noticeable for samples 102, 103, 104, 108, 109, 110 and

111. Furthermore, the fluorine emission decreases prior to reaching the appropriate peak temperature. In contrast, samples 100, 105 and 107 reach their maximum fluorine emission only in the region of the peak temperature and the fluorine emission decreases noticeably only with the beginning of the cooling phase.

Considering the chemically determined fluorine concentrations (see Table 1 as well as Appendix No. CH 3977), the raw materials can be divided into two characteristic types:

(a) raw materials which have a relatively high initial fluorine concentration (about 1000 mg fluorine/kg raw material, including samples 100, 105, 107, 108, 109 and 111 which, on average, emit only about 50% of their fluorine concentration during burning, and

(b) materials which have a relatively low initial fluorine concentration (about 300-700 mg fluorine/kg raw material). These include samples 102, 103 as well as 110 which show, according to the results given in Table 1, only very low amounts of fluorine in the burnt material. This means that almost the entire fluorine concentration has been emitted during burning.

An exception of the above classification is sample 104 which has a relatively high initial fluorine content with 900 mg fluorine/kg unburnt material, but emits only 15% of this fluorine concentration during burning.

The present results have shown that some raw materials have a considerably higher initial fluorine concentration than, for example, those used for brick production in West Germany which, in conjunction with other materials, have an average initial fluorine concentration of about 600 mg fluorine/kg raw material. This is particularly true for samples 100, 107, 108 as well as 109. The other samples correspond in terms of initial fluorine content to the raw materials used by us.

On the basis of relationships between the specific firing curves and the resulting fluorine emission, a series of procedures present themselves which could be used for future reduction of fluorine emission.

(1) The experimental use of additives that may be added to the raw material, such as pulverized glass or slag, and which would allow the reduction of the final firing temperature for certain raw materials.

(2) The experimental use of lime additions, which would retain fluorine in the shards in the form of calcium fluoride and which, according to our experience, can contribute to the reduction of fluorine emission. Samples 102, 107 and 109 may be suitable for this procedure since they have a relatively light fired colour and could possibly tolerate the lightening in colour which would be expected on addition of lime.

(3) The application of technical firing procedures which could determine whether changes in the heating rates, and the lowering of the peak temperature, would have a positive effect on the fluorine emission. It is obvious that the study of these procedures must take into consideration what effects any changes would have on the porosity and strength of the bricks. As an example of the influence of a change in burn temperature on fluorine emission, the two diagrams for sample 109 (from 21 Jan. 1985 and 11 March 1985) may be used. These show that the heating curve for the experimental burn of 21 Jan. 1985, during the period of fluorine-emission time of 1 - 7 hours, was about 30°C lower; this resulted in a considerably reduced fluorine-emission in comparison with the experimental burn of 11 March 1985, with the original heating curve. With respect to the effect of peak temperatures upon fluorine emission, we have found on the basis of other studies carried out in our Institute, that a reduction of about 30 - 50°C can lead to a halving of the fluorine emission which can occur during firing.

Overall, the experimental results have shown that there are possibilities which may lead to a reduction of the fluorine emission considering the various initial fluorine concentrations, as well as the different fluorine emission curves.

The procedures which should be adopted for each specific case (evaluation of additives or technical firing procedures) can only be jointly discussed and determined.

This is required because the procedures to be adopted depend largely on the changes which will be obtained with respect to the desired product qualities, e.g. burn-colour, porosity and strength.

Finally, I would like to point out that the data and observations found can only be applied to the raw materials supplied.

INSTITUT FÜR ZIEGELFORSCHUNG ESSEN E.V.

4300 ESSEN 13, Am Zehnthof 197-203, Telefon 590017-19

PRÜFUNGSBERICHT Nr. KT 2706

Antragsteller:
Ontario Research
Foundation
Mississauga, Ontario
Canada L 5 K 1 B 3
2395 Speakman Drive

Inhalt des Antrages: "Ermittlung des Fluoraustreibungsverhaltens an Original-Ziegeln im Spezialmuffelofen"

Probenahme: Antragsteller

Probeneingang: 20.11.1984 und 12.02.1985 (Probe 111)

Zur Untersuchung lagen vor:

je vier Rohlinge = I 9004 Nr. 100, 102, 103, 104, 105, 107, 108, 109, 110, 111

Gliederung

1. Vorbemerkung
2. Versuchsdurchführung zum Fluoraustreibungsverhalten
3. Fluorgehaltsbestimmung
4. Versuchsergebnisse

1. Vorbemerkung

Das Institut für Ziegelforschung war beauftragt worden, das Fluoraustreibungsverhalten von insgesamt 10 Rohlingen, die in einem Spezialmuffelofen nach den durch den Auftraggeber vorgegebenen Betriebsbrennkurven gebrannt worden waren, zu ermitteln. Zusatzlich erfolgte an den ungebrannten und gebrannten Probeziegeln die Bestimmung der Fluorgehalte durch chemische Analysen. Insbesondere stand hierbei die Beantwortung der Frage im Vordergrund, in welchen Temperaturbereichen der Aufheizzone die Fluoremission bei den verschiedenen Rohstoffen hauptsächlich stattfindet.

2. Versuchsdurchführung zum Fluoraustreibungsverhalten

Die vom Auftraggeber eingereichten verpreßten 10 Ziegelrohlinge wurden zur Bestimmung des Fluoraustreibungsverhaltens in einem elektrisch beheizten gasdichten Spezialmuffelofen nach den vom Auftraggeber gelieferten 10 verschiedenen Betriebsbrennkurven in oxidierender Atmosphäre gebrannt, wobei die Kühlung nach der ofenbedingten Kurve vorgenommen wurde.
Der Wassergehalt der Ofenatmosphäre wurde - wie mit dem Auftraggeber vereinbart - bei allen Bränden mit ca. 30 g/kg trockener Luft eingestellt und über den gesamten Brennverlauf konstant gehalten.

Die Fluorgehalte in den Abgasen und die Brenntemperaturen wurden während der Brände kontinuierlich registriert. Mittels eines Computers wurden diese Daten unter Berücksichtigung des Luftdurchsatzes und der verschiedenen Brenngewichtsverluste auf folgende Größen umgerechnet:

a) Fluoraustreibungsrate (Fluor-Emission-Rate), angegeben in mg Fluor/kg · h, welche ausweist, wieviel mg Fluor pro kg gebrannter Ware und Stunde bei der jeweiligen Temperatur ausgetrieben werden.

b) Integrale Fluoraustreibung (Integral-Fluor-Emission) in den Einheiten mg Fluor/kg gebrannter Ware, welche ausweist, wieviel mg Fluor pro kg gebrannter Ware bis zur jeweiligen Temperatur ausgetrieben worden sind.

Von einem an den Computer angeschlossenen Zeichengerät wurden neben der Brenntemperatur die unter a) und b) genannten Größen über der Brennzeit in entsprechenden Diagrammen grafisch dargestellt. Hier sei noch darauf hingewiesen, daß in den Bildern nur die Zeit ab Beginn bis zum Ende der Fluor-Emission (Time of Fluor-Emission) dargestellt worden ist. Die Ergebnisse der mit den Probeziegeln durchgeführten Versuchsbrände sind in den Bildern 1 - 10 wiedergegeben.

-3-

3. Fluorgehaltsbestimmung

Die Ergebnisse der an den ungebrannten und gebrannten Probeziegeln durchgeführten chemischen Fluorgehaltsbestimmungen sind dem Anhang (Prüfungsbericht Nr. CH 3977) zu entnehmen.

4. Versuchsergebnisse

Zunächst ist zu bemerken, daß dem Institut für Ziegelforschung etwaige Angaben, die zur Rohstoffcharakteristik dienen könnten, wie chemische Voll- und röntgenographische Mineralanalysen der Rohstoffe, nicht zur Verfügung standen. Desweiteren lagen dem Institut keine Daten über Produkteigenschaften, wie beispielsweise Wasseraufnahme und Scherbenporosität der gebrannten Materialien vor, die bekanntermaßen einen erheblichen Einfluß auf die Fluor-Emission ausüben können.

Die Ergebnisse zur Ermittlung des Fluoraustreibungsverhaltens im Spezialmuffelofen des Insituts der vom Auftraggeber angelieferten 10 Original-Rohlinge sind aus den Bildern 1 - 10 zu entnehmen. Hiernach läßt sich zunächst feststellen, daß die Fluor-Emission bei den meisten hier untersuchten Probeziegeln bei Temperaturen von 700 - 750°C im Bereich der Aufheizzone beginnt, was für die Proben 100, 102, 103, 104, 105, 108, 109 und 110 zutrifft. Lediglich bei den Proben 107 und 111 setzt die Fluor-Emission erst bei ca. 800°C ein. Sicherlich ist hier zu bemerken, daß der Beginn der Fluor-Emission u.a. davon abhängig ist, mit welcher Aufheizgeschwindigkeit der jeweilige Ziegel bis zum Beginn der Fluor-Emission aufgeheizt worden ist.

Bei weiterer Betrachtung der Kurven für die Fluor-Emission fällt auf, daß die meisten Probeziegel das Maximum ihrer Fluor-Emission bereits vor Beginn der Spitzentemperatur erreichen, was insbesondere bei den Proben 102, 103, 104, 108, 109, 110 sowie 111 deutlich wird. Weiterhin nimmt die Fluor-Emission hier vor Erreichen der jeweiligen Spitzentemperatur bereits wieder ab. Im Gegensatz dazu erreichen die Proben 100, 105 und 107 ihr Maximum der Fluoraustreibung erst im Bereich der Spitzentemperatur und erst mit Beginn der Kühlphase nimmt hier die Fluor-Emission erheblich ab.

Ausweislich der chemisch bestimmten Fluorgehalte (s. Tabelle 1 sowie Anhang Nr. CH 3977) läßt sich feststellen, daß die Rohstoffe im wesentlichen in zwei charakteristische Typen einzuteilen sind:

a) Rohstoffe, die einen relativ hohen Anfangsfluorgehalt im Rohmaterial besitzen (ca. 1000 mg Fluor/kg ungebranntes Material), hierzu zählen die Proben 100, 105, 107, 108, 109 und 111, die vergleichsweise im Mittel nur etwa 50 % ihres anfänglichen Fluorgehaltes beim Brand emittieren und

b) solche, die einen vergleichsweise mittleren Anfangsfluorgehalt im Rohmaterial besitzen (ca. 300 - 700 mg Fluor/kg ungebranntes Material). Hierzu zählen die Proben 102, 103 sowie 110, die jedoch ausweislich der Analysenergebnisse in Tabelle 1 nur noch sehr geringe Restfluorgehalte im gebrannten Material aufweisen, was hier bedeutet, daß nahezu der gesamte anfänglich vorhandene Fluorgehalt beim Brand emittiert worden ist.

Eine Ausnahme von der hier vorgenommenen Einteilung bildet die Probe 104, die zwar auch mit ca. 900 mg Fluor/kg ungebranntes Material einen relativ hohen Anfangsfluorgehalt besitzt, beim Brennen jedoch nur ca. 15 % dieses Anfangsfluorgehaltes emittiert.

Die hier vorliegenden Ergebnisse haben insgesamt gezeigt, daß einige Rohstoffe bezüglich ihres Anfangsfluorgehaltes vergleichsweise erheblich höher liegen als beispielsweise solche, die in der Bundesrepublik Deutschland zur Mitverziegelung anstehen und hier im Mittel einen Anfangsfluorgehalt von ca. 600 mg Fluor/kg ungebranntes Material aufweisen. Dies trifft in besonderem Maße für die Proben 100, 107, 108 sowie 109 zu. Die übrigen hier untersuchten Proben entsprechen bezüglich ihres Anfangsfluorgehaltes denen bei uns eingesetzten Rohstoffen.

Aufgrund der hier gefundenen Zusammenhänge zwischen den jeweils vorgegebenen Brennkurven und den daraus resultierenden Fluor-Emissionen bieten sich jedoch eine Reihe von Maßnahmen an, die zukünftig zu einer Fluor-Emissions-Minderung beitragen könnten:

1.) Etwa die Erprobung von Zusätzen, die dem Ziegelrohstoff beigemischt werden, wie Glasmehle oder Schlackenmehle, die es ermöglichen würden, bei bestimmten Rohstoffen die Garbrandtemperatur herabzusetzen.

2.) Die Erprobung von Kalkzugaben, die das Fluor z.B. in Form von Calciumfluoriden im Scherben zurückhalten würden und nach unseren Erfahrungen zu einer Fluor-Emissions-Minderung beitragen könnten. Für derartige Maßnahmen würden sich beispielsweise die Proben 102, 107 und 109 anbieten, da diese bereits eine helle Brennfarbe aufweisen, so daß hier eine Brennfarbenaufhellung, die bei Kalkzugabe zu erwarten ist, möglicherweise toleriert werden könnte.

3.) Durch brenntechnische Maßnahmen, indem erprobt werden könnte, inwieweit Veränderungen in den Aufheizgeschwindigkeiten bzw. Herabsetzung der Spitzentemperaturen positive Einflüsse auf die Fluor-Emission bewirken. Selbstverständlich muß bei Erprobung derartiger Maßnahmen immer berücksichtigt werden, welche Einflüsse sich auf die Produkteigenschaften wie Porosität und Festigkeit der Ziegel ergeben. Als Beispiel dafür, wie sich etwa eine veränderte Brennführung auf die Fluor-Emission insgesamt auswirken kann, seien die beiden Diagramme der Probe 109 (vom 21.01.1985 und vom 11.03.1985) betrachtet. Demnach ergibt sich hier, daß aufgrund der Tatsache, daß die Brennkurve im Bereich der Fluor-Emissionszeit von 1 - 7 Stunden beim Versuchsbrand vom 21.01.1985 insgesamt um ca. 30 °C niedriger lag, eine erheblich verminderte Fluor-Emission im Vergleich zu dem am 11.03. mit der Original-Brennkurve gefahrenen Versuchsbrand. Bezüglich des Einflusses der Spitzentemperaturen auf die Fluor-Emission hat sich aufgrund von Untersuchungen, die in anderen Zusammenhängen im Institut bereits durchgeführt worden sind, gezeigt, daß eine Absenkung um ca. 30 - 50 °C in einigen Fällen zu einer Halbierung der beim Brand auftretenden Gesamtfluor-Emission führen kann.

Insgesamt gesehen haben die Untersuchungsergebnisse gezeigt, daß sowohl aufgrund der vorliegenden recht unterschiedlichen Anfangsfluorgehalte als auch der verschiedenen Fluor-Emissions-Kurven für die Zukunft Möglichkeiten bestehen, die eine Fluor-Emissionsminderung erwarten lassen.

Welche Maßnahmen im speziellen, real für jeden hier vorliegenden Einzelfall zu ergreifen sind (Erprobung von Massezusätzen oder brenntechnische Maßnahmen), kann letztlich nur gemeinschaftlich diskutiert und festgelegt werden.
Dies ist deshalb erforderlich, weil die zu ergreifenden Verfahrensschritte weitgehend davon abhängen, inwieweit sich im Hinblick auf die jeweils gewünschten Produktqualitäten, wie z.B. Brennfarbe, Porosität und Festigkeit, Veränderungen ergeben werden.

Abschließend sei der Hinweis gestattet, daß sich die gefundenen Daten und Erkenntnisse naturgemäß nur auf die eingereichten Rohstoffproben beziehen können.

Essen, den 22.03.1985
Dr.Ha-schw

Der Institutsleiter:

(Dipl.-Ing. K. Fossum)

Der Sachbearbeiter:
Dr. Hauck
(Dipl.-Phys. Dr. Hauck)

Anlage zu KT Nr. 2706

Tabelle 1

Results of the chemical Analyses:

Fluor Contents of the Raw and Burned Materials and calculated Fluor-Emission in Milligramm Fluor per Kilogramm Burned Brick.

Sample Number	Fluor-Contents (mg Fluor/kg)		Fluor-Emission (mg Fluor/kg)
	Raw Material	Burned Material	
100	1137	517	620
102	332	46	286
103	690	70	620
104	930	790	140
105	890	610	280
107	1150	580	570
108	1060	670	390
109	1098	488	610
110	560	20	540
111	790	331	459

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 31 g/Kg TROCKENER LUFT . PROBE NR. 100

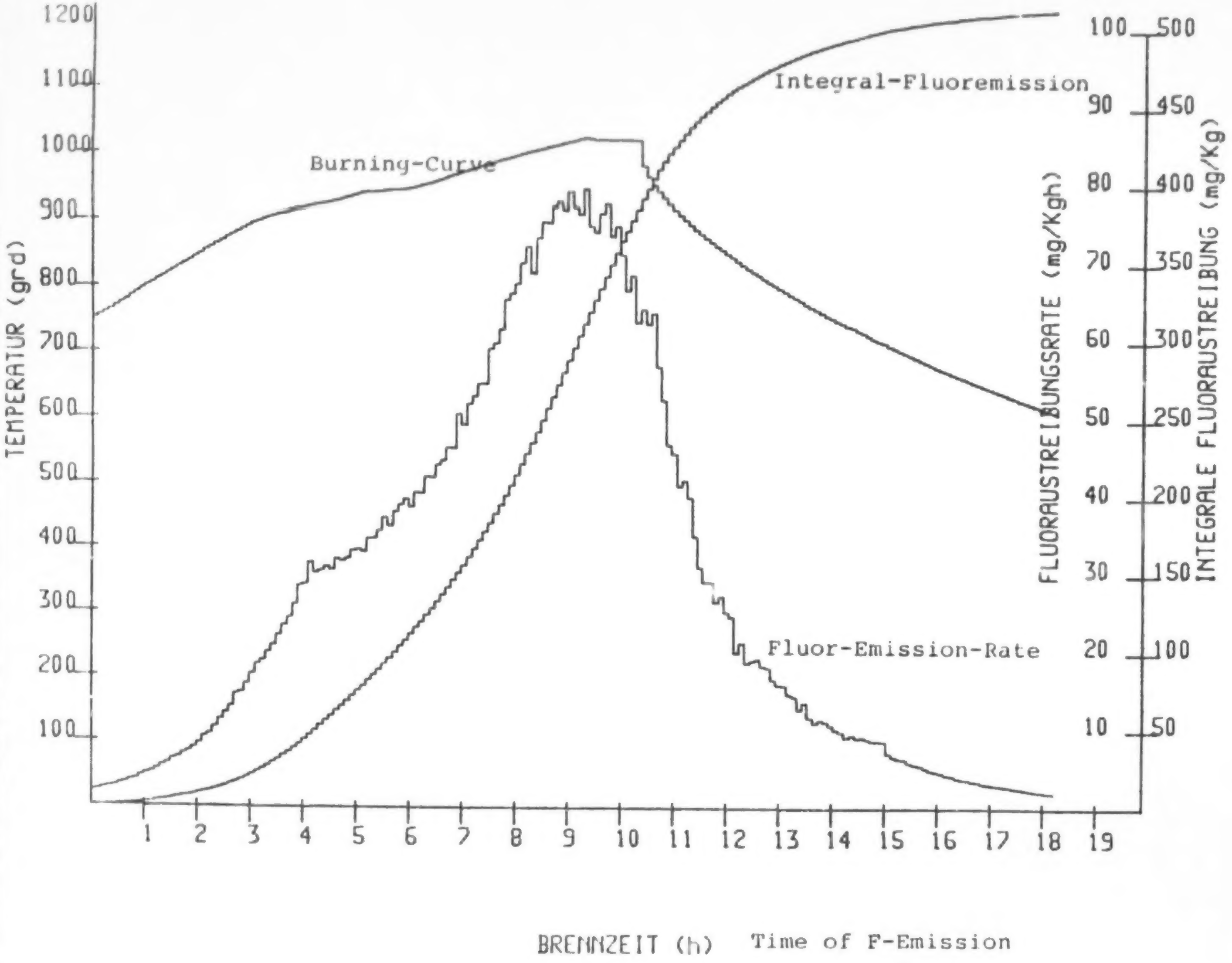
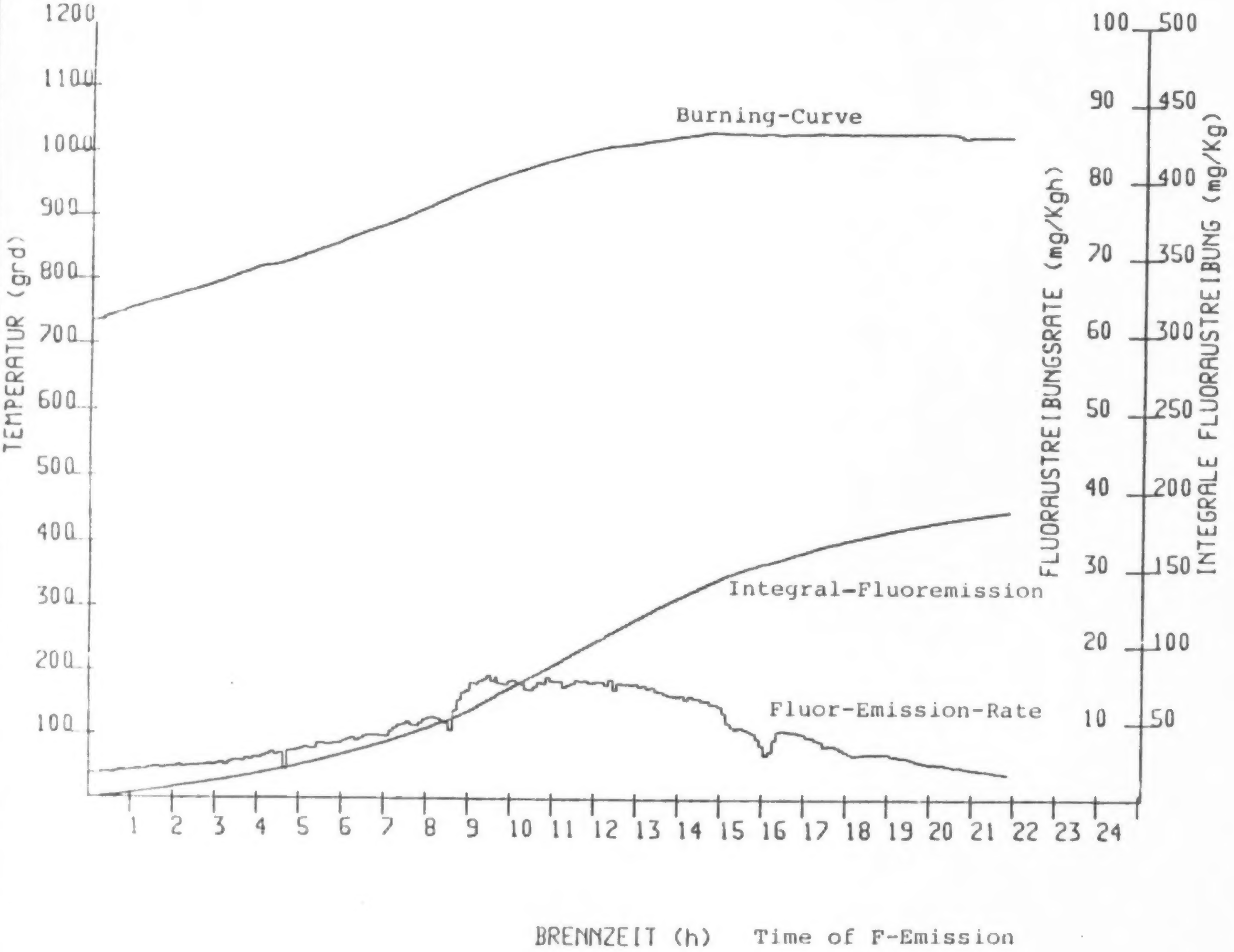


Bild 1

Dat.:29.11.1984
KT2706.2



FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

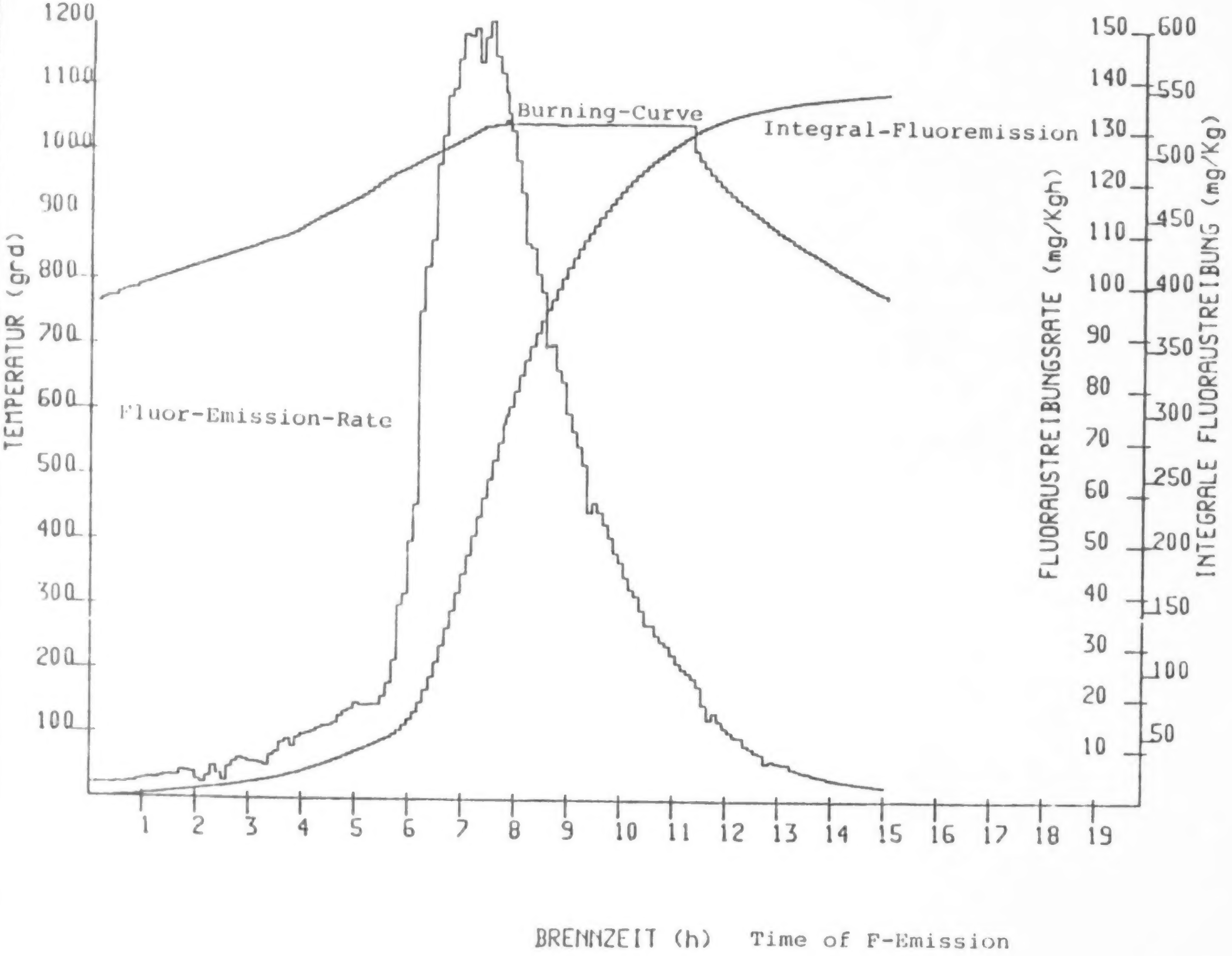
PROBE NR.: 102

Dat.: 10.12.1984
KT2706.5

Bild 2

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE NR.:103



Dat.:16.01.1985
KT27061.1

Bild 3

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 30 g/Kg TROCKENER LUFT

PROBE NR.: 104

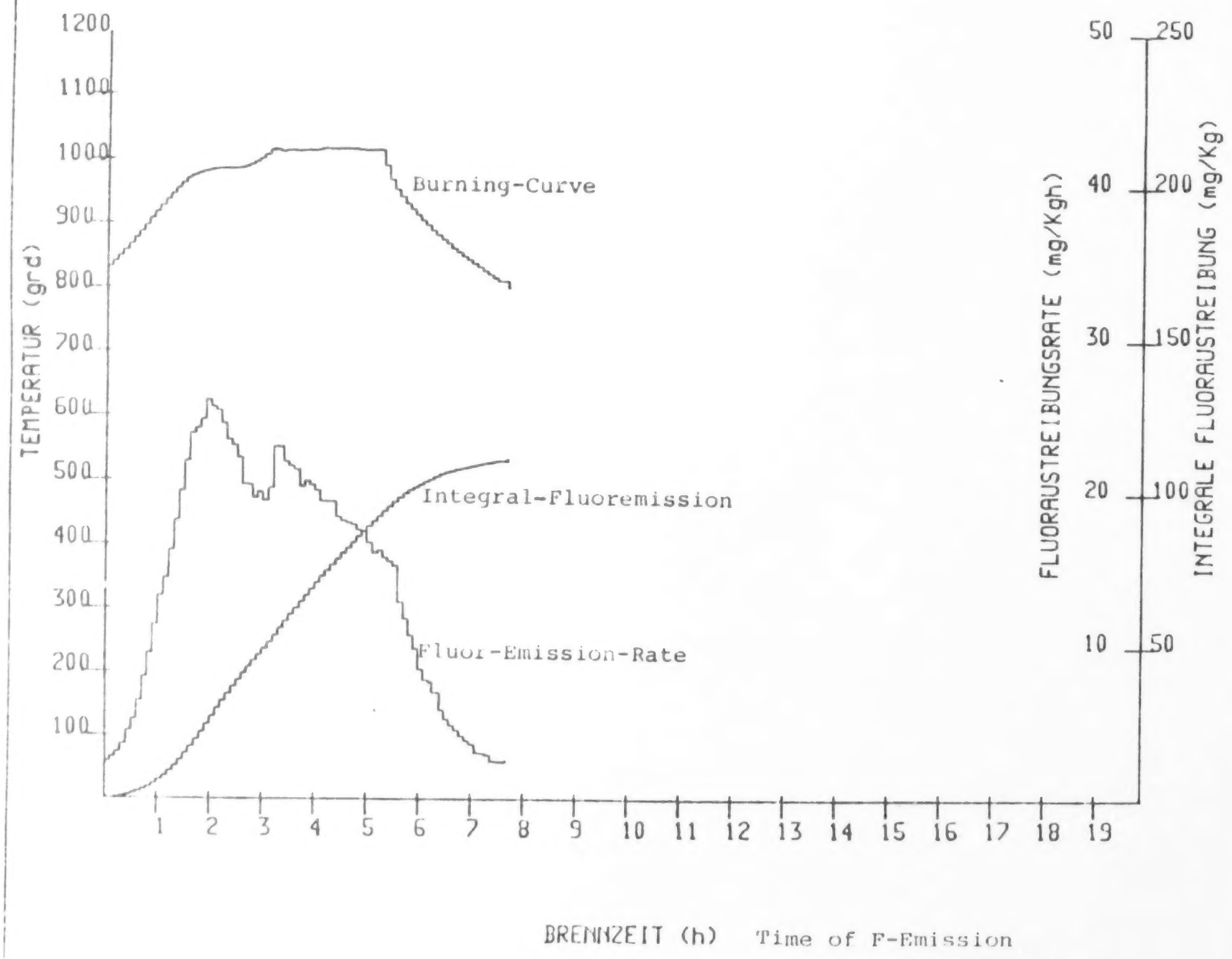


Bild 4

Dat.: 13.12.1984
KT2706.6

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

PROBE NR.: 105

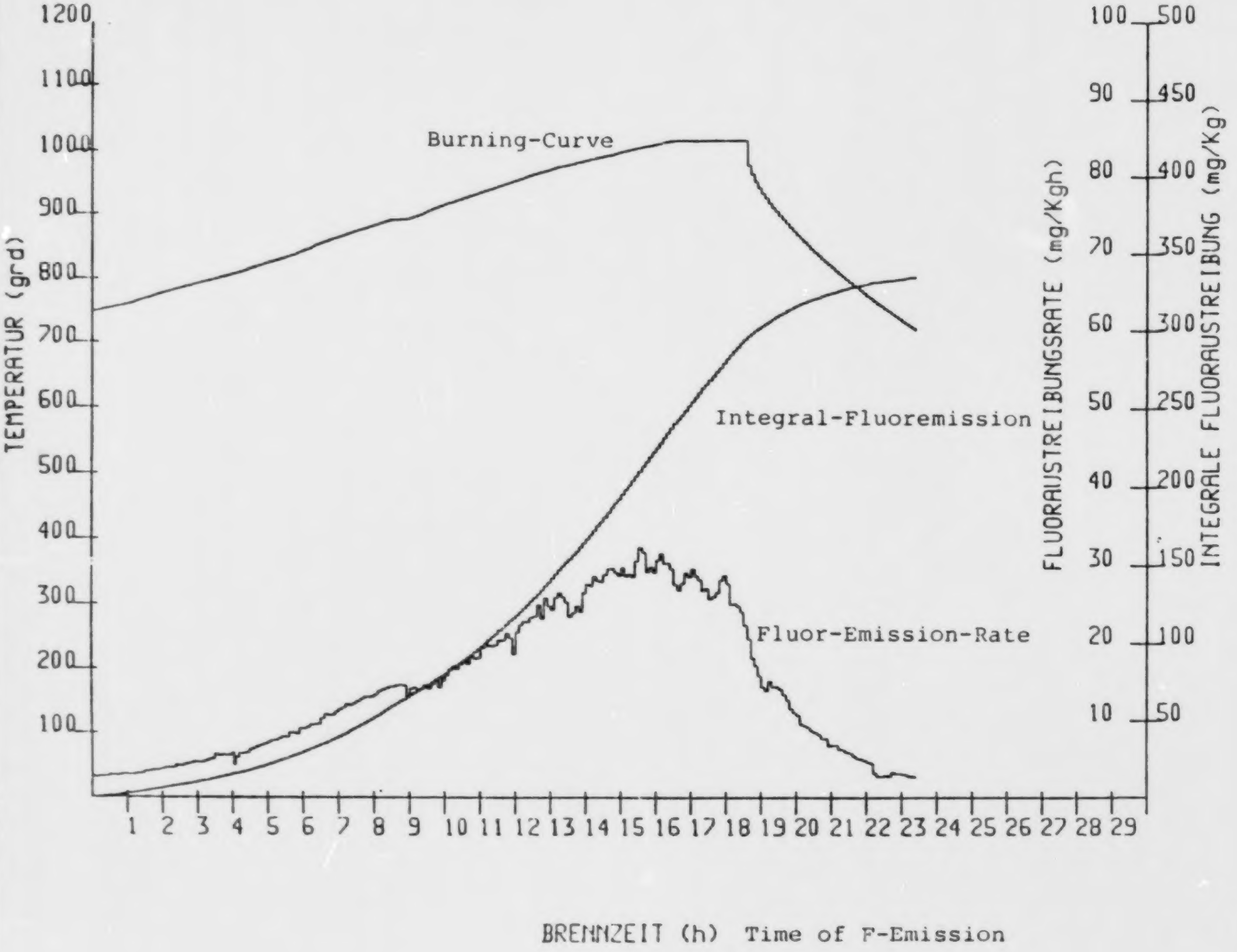


Bild 5

Dat.: 20.12.1985
KT2706.8

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE NR.: 107

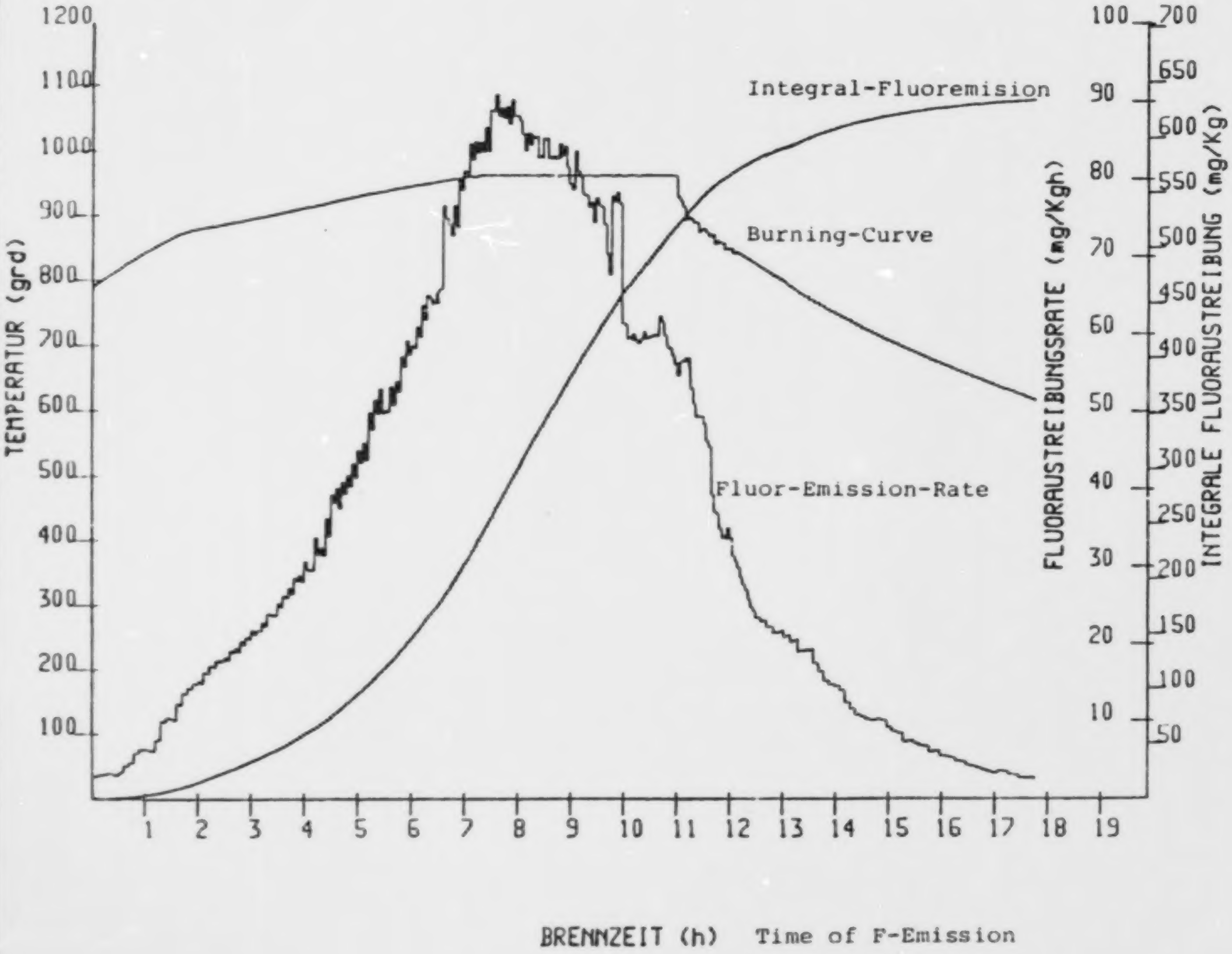


Bild 6

Dat.:23.01.1985
KT27061.3

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE NR.:108

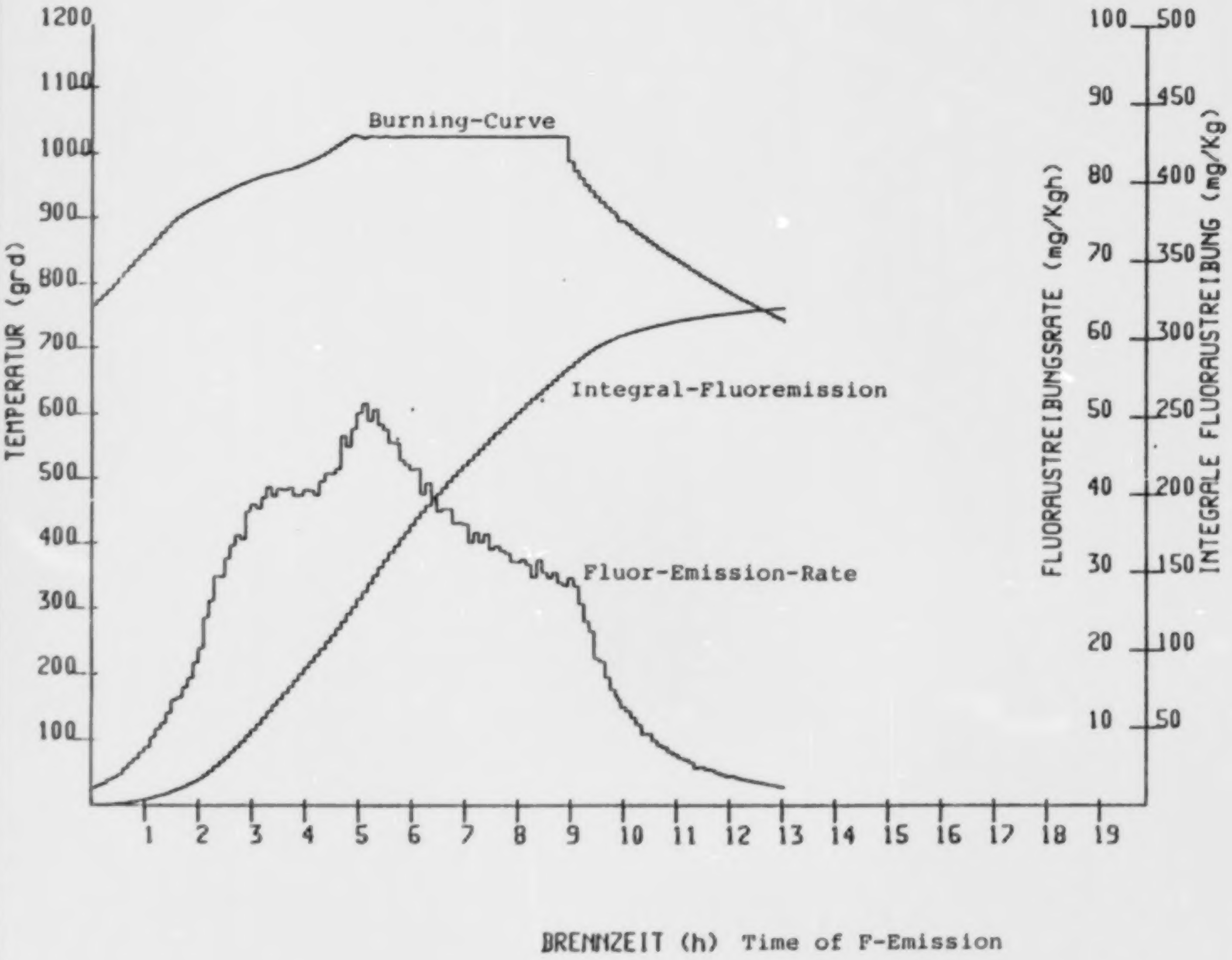


Bild 7

Dat.:03.12.1984
KT2706.3

Bild 8

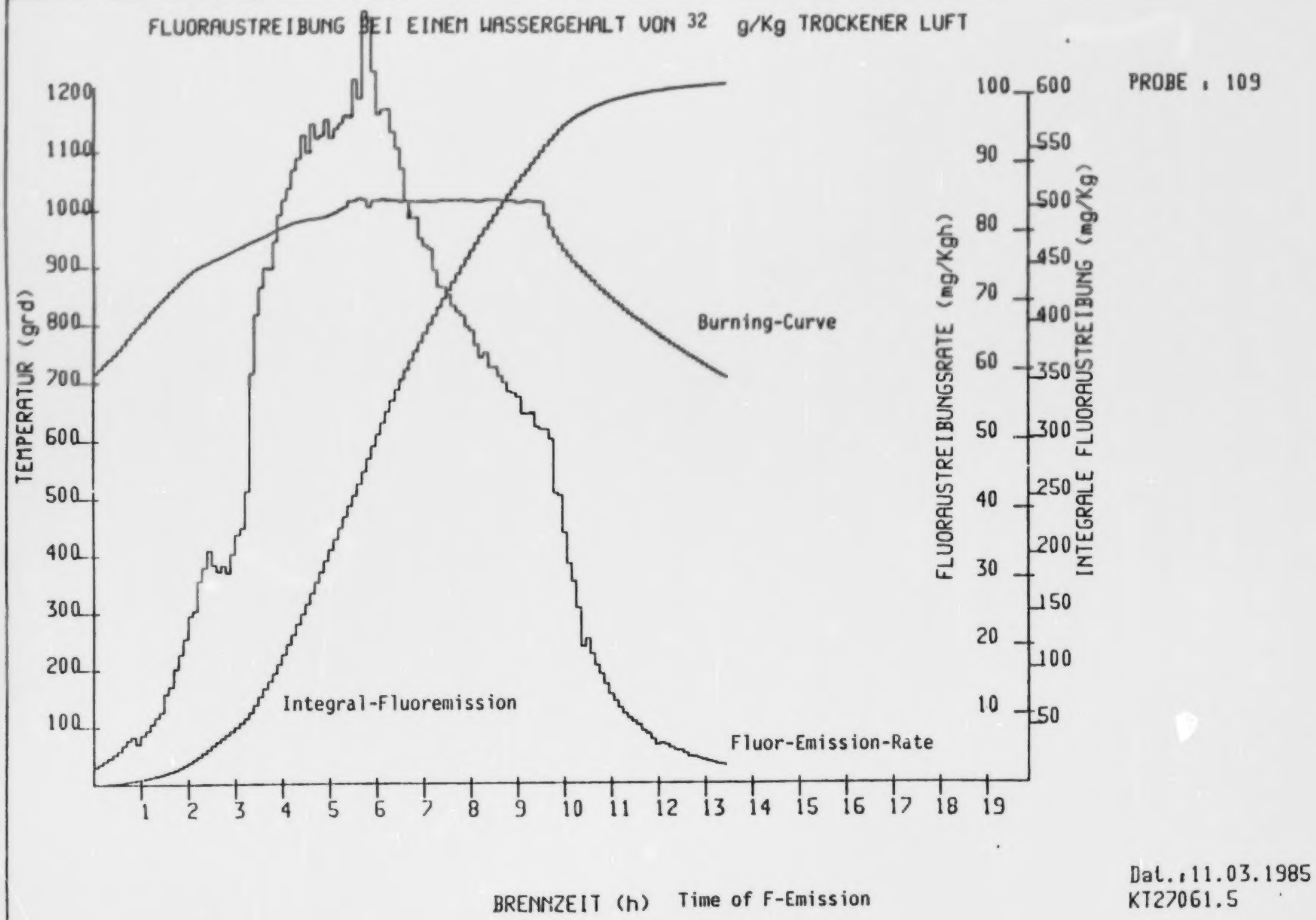
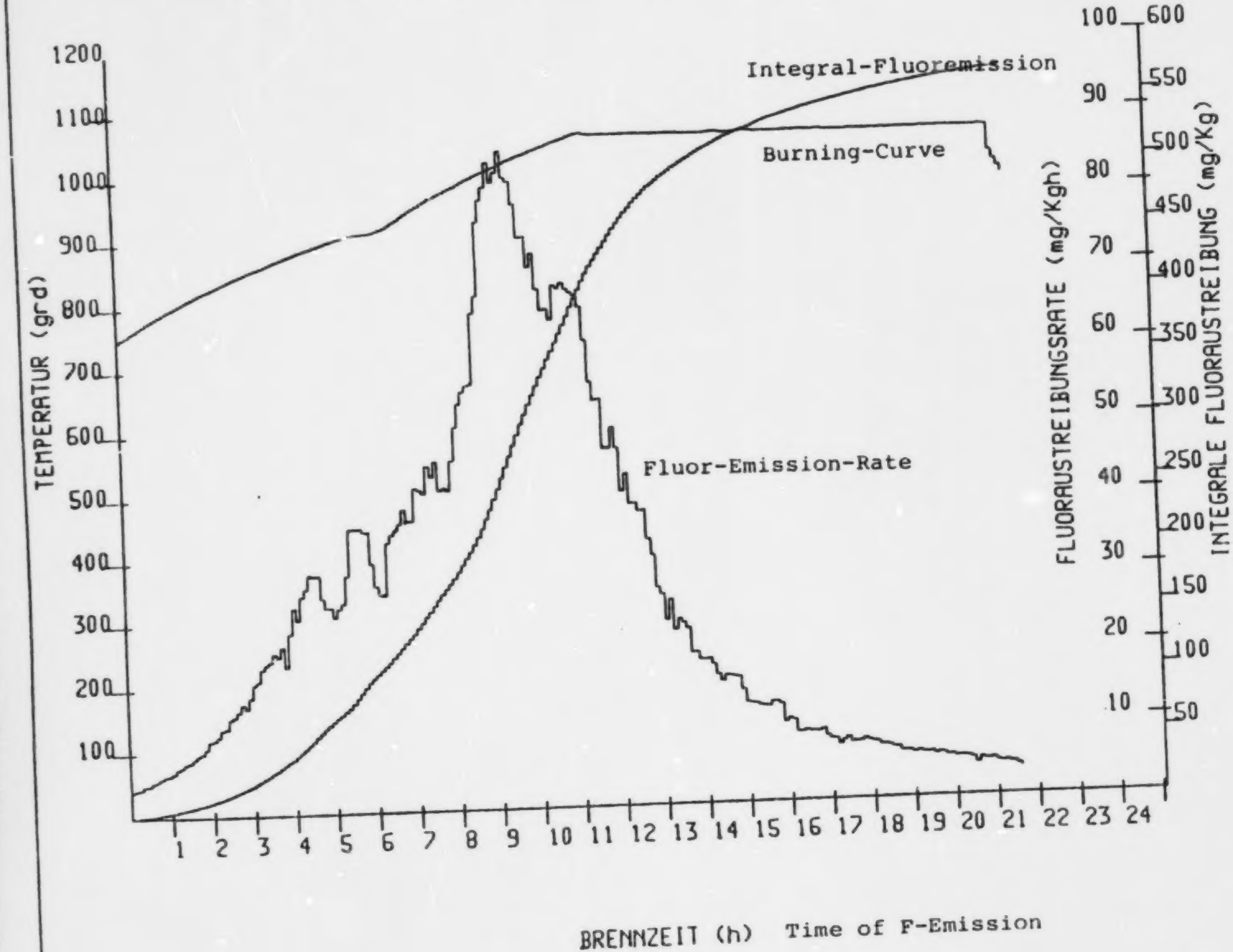

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT
PROBE : 109
TEMPERATUR (grd)
1200
1100
1000
900
800
700
600
500
400
300
200
100
FLUORAUSTREIBUNGSRATE (mg/Kgh)
100
90
80
70
60
50
40
30
20
10
INTEGRALE FLUORAUSTREIBUNG (mg/Kg)
600
550
500
450
400
350
300
250
200
150
100
50
Burning-Curve
Integral-Fluoremission
Fluor-Emission-Rate
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
BRENNZEIT (h) Time of F-Emission
Dat.:11.03.1985
KT27061.5

Bild 9

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 33 g/Kg TROCKENER LUFT

PROB NR.:110



Dat.:10.01.1985
KT2706.9

FLUORAUSTREIBUNG BEI EINEM WASSERGEHALT VON 32 g/Kg TROCKENER LUFT

PROBE :111

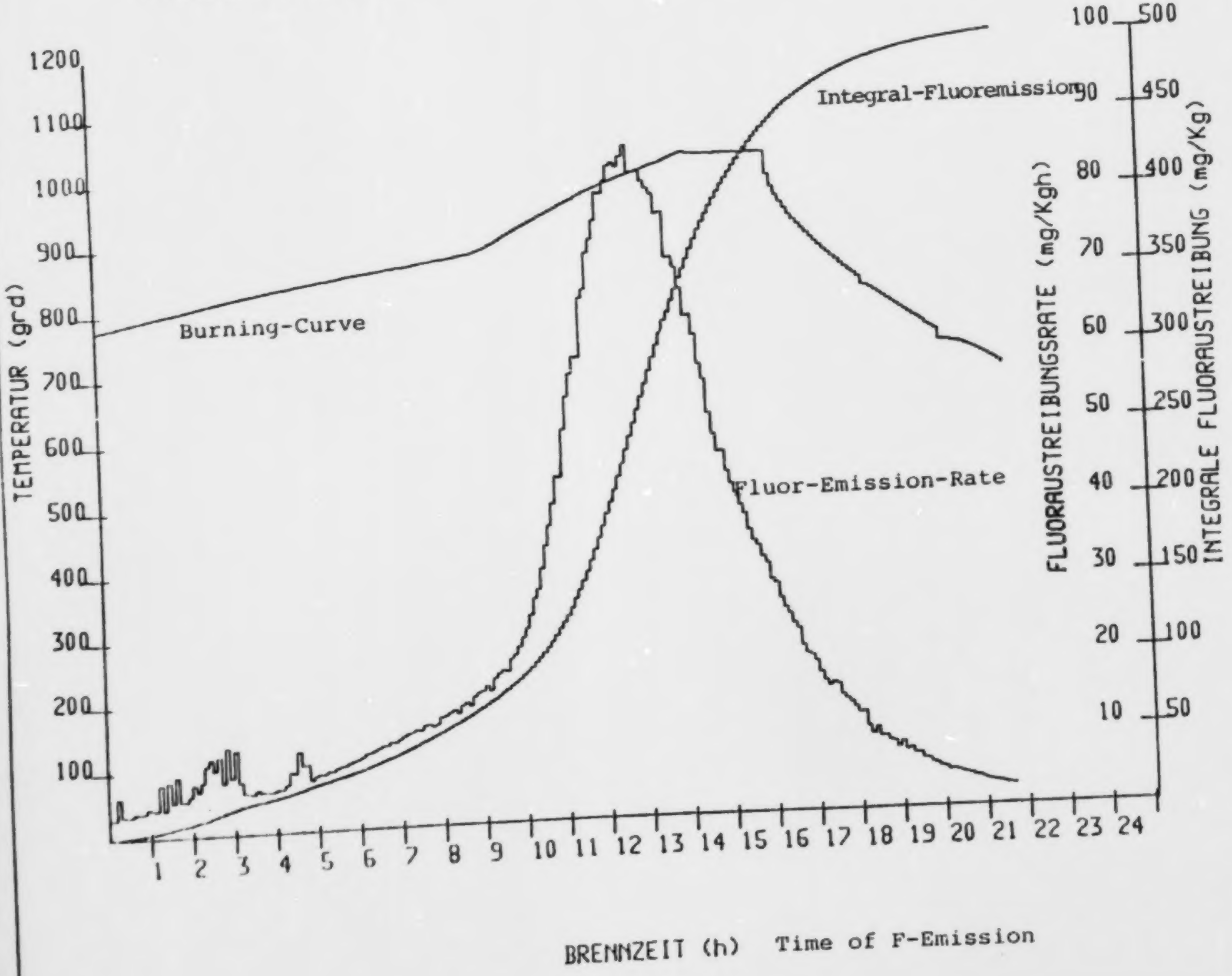


Bild 10

Dat.:25.02.1985
KT27061.4

INSTITUT FÜR ZIEGELFORSCHUNG ESSEN E.V.
Am Zehnthof 197-203, 4300 ESSEN 13, Telefon 59 00 17-19

PRÜFUNGSBERICHT Nr. CH 3977

(Anhang zum Prüfungsbericht Nr. KT 2706)

Antragsteller: Ontario Research Foundation
Mississauga, Ontario

Inhalt des Antrages: Bestimmung des Fluorgehaltes in gebrannten und ungebrannten Ziegeln

Probeneingang: 29.11.84 bis 28.1.85

Probenentnahme: Antragsteller

Probenbezeichnung:

Ein Ziegelrohling Nr. 100	P 6979
Ein halber Ziegel Nr. 100	P 6999
Ein Ziegelrohling Nr. 102	P 6980
Ein halber Ziegel Nr. 102	P 7000
Ein Ziegelrohling Nr. 103	P 6981
Ein halber Ziegel Nr. 103	P 7005
Ein Ziegelrohling Nr. 104	P 6982
Ein halber Ziegel Nr. 104	P 7001
Ein Ziegelrohling Nr. 105	P 6983
Ein halber Ziegel Nr. 105	P 7002
Ein Ziegelrohling Nr. 107	P 6984
Ein halber Ziegel Nr. 107	P 7006
Ein Ziegelrohling Nr. 108	P 6985
Ein halber Ziegel Nr. 108	P 7003
Ein Ziegelrohling Nr. 109	P 6986
Ein halber Ziegel Nr. 109	P 7007
Ein Ziegelrohling Nr. 110	P 6987
Ein halber Ziegel Nr. 110	P 7004
Ein Ziegelrohling Nr. 111	P 7009
Ein halber Ziegel Nr. 111	P 7010

Durchführung und Ergebnisse der Untersuchung

Um die Differenz zwischen dem Fluorgehalt des Rohmaterials und des gebrannten Materials bilden zu können, müssen auch die Anteile im Rohmaterial auf den gebrannten (glühverlustfreien) Zustand bezogen werden. Um diese Umrechnung vornehmen zu können, wurde in der Rohmaterialprobe zusätzlich der Glühverlust (1000 °C) + Restfeuchte ermittelt.

Die Bestimmung des Fluorgehaltes wurde durch pyrohydrolytische Abtrennung nach dem in der Technischen Überwachung 7 (1966) Nr. 10 beschriebenen Verfahren und anschließender kolorimetrischer Bestimmung in Anlehnung an die VDI-Richtlinie 2452 vom Dezember 1963 vorgenommen.

Je als Mittelwert zweier Bestimmungen enthielten die Proben folgende Anteile in Massenprozent:

	Fluorgehalt (ungebrannt)	Glühverlust	Fluorgehalt (bez.a.gebrannt)	Fluorgehalt (gebrannt)	Diff.
P 6979 (100 roh)	0,106	6,62	0,114		
P 6999 (100)				0,052	0,062
P 6980 (102 roh)	0,031	7,30	0,033		
P 7000 (102)				0,005	0,028
P 6981 (103 roh)	0,065	5,93	0,069		
P 7005 (103)				0,007	0,062
P 6982 (104 roh)	0,086	8,04	0,093		
P 7001 (104)				0,079	0,014
P 6983 (105 roh)	0,083	7,15	0,089		
P 7002 (105)				0,061	0,028
P 6984 (107 roh)	0,106	7,71	0,115		
P 7006 (107)				0,058	0,057

	Fluorgehalt (ungebrannt)	Glühverlust	Fluorgehalt (bez.a.gebrannt)	Fluorgehalt (gebrannt)	Diff.
P 6985 (108 roh)	0,096	8,95	0,106		
P 7003 (108)				0,067	0,039
P 6986 (109 roh)	0,095	13,24	0,110		
P 7007 (109)				0,097	0,013
P 6987 (110 roh)	0,052	7,43	0,056		
P 7004 (110)				0,002	0,054
P 7009 (111 roh)	0,075	4,49	0,079		
P 7010 (111)				0,033	0,046

Die Ergebnisse gelten nur für die untersuchten Proben.

Essen, den 12.03.1985
pa-bo

Der Institutsleiter:

(Dipl.-Ing. K. Fossum)

Der Sachbearbeiter:

(Dipl.-Chem. Pauls)

APPENDIX 2

Automatic Fluoride Analysis
- Brochures and Information on
Bran & Lubbe 'Sensimeter G

JAN 8 1985

Ontario Research
Attn. Mr. I.H. Joyce
Mississauga,
Ontario, Canada L5K1B3

January 2nd, 1985
AP Ad/He
Dipl.-Phys. Adomeit

HF-Emission control
- our project 53 o89 428 -

Dear Mr. Joyce,

we refer to your letter of the 3rd od December and are pleased by your attention for our B&L Sensimeter G.

The Sensimeter G is approved by government for the monitoring of fluoride or chloride in stack gases. It is mainly used in refuse incinerations plants.

Some of it's characteristic features are:

- selective monitoring of fluoride
- negligible interferences against common constituents and H_2O
- internal calibration with standard solution. No gases neccessary.

The sampling system is an important part of the whole system. It is completly temperature controlled to avoid condensation.

Please use the data sheets for more information. We like to mentions our B&L Ecometer in this case too. It is designed for monitoring stack gases too. But it operates continuously

- 2 -

and offers a very short response time for controlling the gas purification. For your information we enclose a data sheet about the B&L Ecometer too.

B&L has a representative in Canada as well a branch in the U.S. A.

in Canada: GENEQ inc.
7978 Jarry St. East
Anjou, Quêbec H1J1H5

phone: 001514 - 354 2511
Telex: 0215-829568 geneq mtl

in USA: Bran & Luebbe, Inc.
512 Northgate Parkway
Wheeling, Illinois 6oo9o

phone: 001 - 312-520-0700
Telex: 023-072 6427 Branlubbe whlg

If you need more information about our gas analyzers or any other product of our program, please let us known.

Best Regards

Bran & Luebbe GmbH
Analyzer Department

Encl.

a
t
2o7

BRAN & LUEBBE

Analysengeräte
Montage und Bedienung

Industrial analysers
Installation and operation

Installation et opération

Typ B&L Sensimeter G Fab.Nr. 53 14318

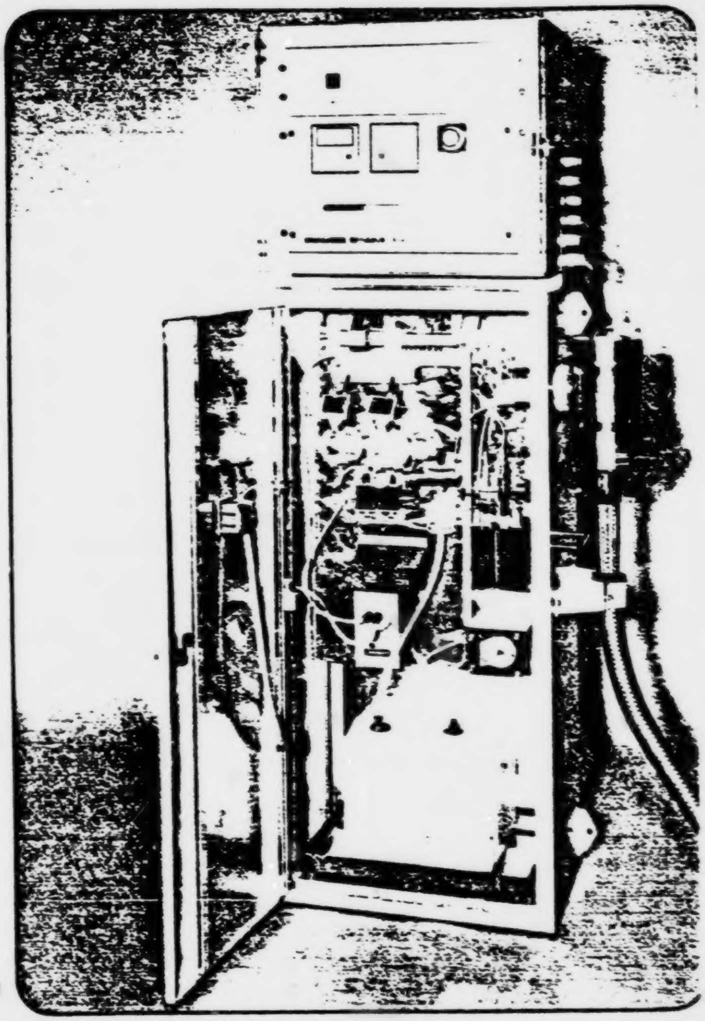
BRAN & LUBBE
POSTFACH 1360 · 2000 NORDERSTEDT 1 · TELEFON (040) 52 20 21 · TELEX 02 174 881 · TELEGRAMM DOSIERPUMPE HAMBURG

Analysis of Gases

Sensimeter G

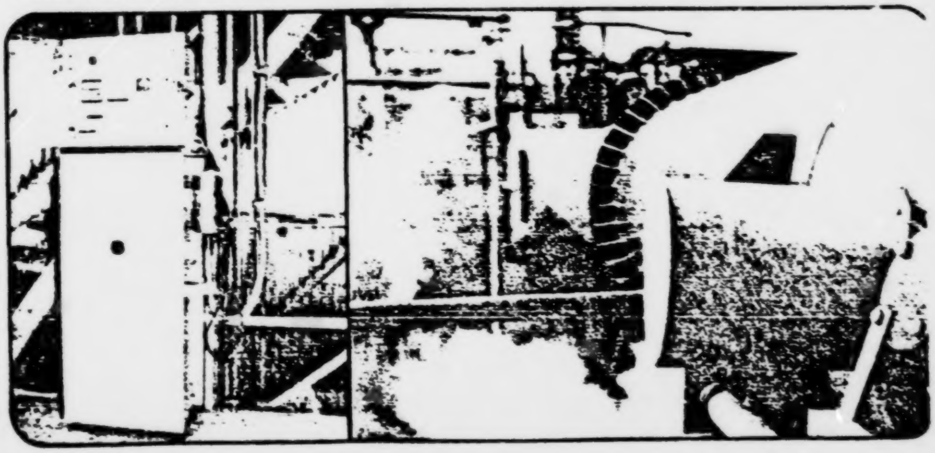
Measured Components:
Hydrogen Chloride – HCl and
Hydrogen Fluoride – HF

Notwithstanding the considerable care taken by industry when discharging flue and waste gases, enormous amounts of pollutants enter the atmosphere. Gas purification plants and procedures are constantly being optimised; however the use of continuous monitoring devices has become indispensible. Such devices can immediately recognize exceeded limits and initiate instantaneous countermeasures. The Sensimeter G operates with an ion-selective electrode as detector. Metered discontinuously in precise volumes in six-minute cycles, the buffer solution is continuously permeated by the indrawn gaseous sample so that the measured component is absorbed by the buffer solution. The enriched buffer solution is cyclically fed to the measuring cell. Thus, a potential proportional to the concentration arises which subsequent to amplification, forms the output signal. Suited for installation in industrial workrooms, the device has a rugged construction in which the analyzer and the measurement and control unit are completely separated and sealed one against the other. Together with the sampling system, the device has been tested by the Technical Standards Office and recommended as a measuring apparatus for monitoring according to the Federal Emissions Control Law for the monitoring of refusal incineration plants, aluminium mills, and sintering plants.



Sensimeter G with sample taking probe (photo on right) for emissions monitoring at a refusal incineration plant.

Technical Data
Integrated
Calibration System
Sampling Connection
for B&L Gas Tapping System
(Approved by Technical
Inspection Office)
Accuracy:
± 6%
Measuring Signal:
0 . . . 20 mA,
4 . . . 20 mA



BRAN & LÜBBE
Analysentechnik

Environmental Protection

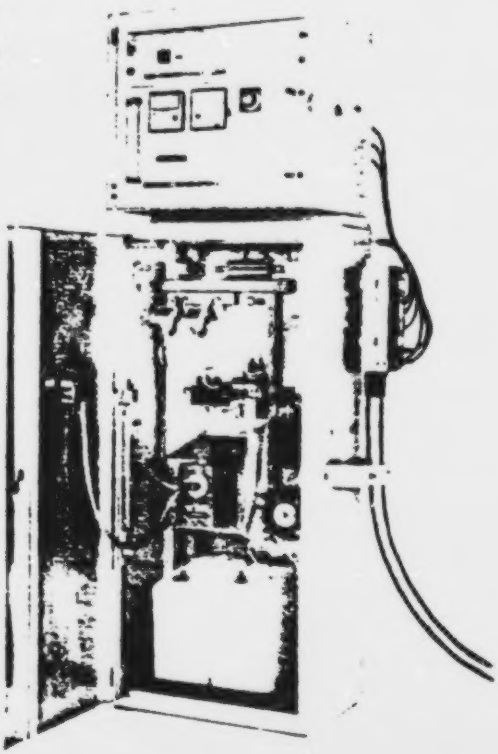
AI 61.3 E - 0883
B&L Sensimeter G

B&L SENSIMETER G Analyzing System

for the continuous emission monitoring of

hydrogen fluoride HF
hydrogen chloride HCl

in dry and moist gases



Features:

- well arranged control and analyzer modules
- rugged gas sampling system
- convenient maintenance
- integral calibrating system
- excellent availability
- tested and approved as emission analyzer by the Ministry of the Interior, FRG

The B&L SENSIMETER is used for monitoring automatically process and waste gases. The ion-sensitive electrodes are selected acc. to the particular application.

The gaseous sample is supplied continuously to the system through a heated sampling system (probe, filter, sampling line). The compound to be analyzed is absorbed in an aqueous buffer solution. Subsequently, the ionic concentration of the solution is measured under controlled conditions by an ion-sensitive electrode.

A program timer serves to control all functions of the system, from dispensing controlled volumes of buffer solution up to the instrument read-out.

Typical applications

Sludge and refuse incineration plants with or without gas purification systems
Aluminium smelters
Iron and steel mills
Glass and ceramics industries
Stoneware industry, brickworks
Fertilizer plants

Hydrogen chloride (inorganic gaseous chlorine compounds)	5	-	500 mg/Sm³ HCl
	10	-	1000 mg/Sm³ HCl
	30	-	3000 mg/Sm³ HCl
	200	-	20000 mg/Sm³ HCl
Hydrogen fluoride (inorganic gaseous fluorine compounds)	0.2	-	20 mg/Sm³ HF
	0.5	-	50 mg/Sm³ HF
	1.0	-	1000 mg/Sm³ HF

Scope of supply:

Instrument cabinet	For analyzer unit, control and power unit, rugged metal housing with doors, all surfaces with paint finish.
Analyzer unit	Gas and buffer solution dispensing systems, thermostated measuring cell with ion-sensitive measuring chain, calibrating and buffer solution storage vessels, effluent collecting vessel, electrically heated dust filter with sample connection for the gas sampling system.
Control and power unit	Potential measuring amplifier with read-out, test outlet and connection for external recorder, program timer for the analyzer functions, fault and status signals, temperature controller for the gas sampling system with switch and fuses.

Specs and data:

Sample waste gas at sampling point	
pressure difference (against atm)	±25 mbar, or requirement
temperature	293 - 673 K (20 - 400°C)
flow rate	40 - 70 l/hr
dust	selection of filter corresponding to measuring gas max. 20 g/m³
water content	max. 50 Vol.% H_2O
Sample connection for	B&L Gas Sampling System (approves by Ministry of the Interior)
Reagent storage	plastic vessel, 10 l
Reagent discharge	plastic vessel, 10 l
Accuracy	± 10% of read-out
measuring display	analogue, scale division logarithmic
measuring signal	0 - 20 mA, max. burden 500 ohm, logarithmic 4 - 20 mA, on request linear, on request
Limit signal	(high) no-voltage switch-over contact, load 60 V, 2 A, 80 VA
Power supply	220 V ± 10 %, 50 Hz
Power consumption	150 VA, without sampling system
Enclosure	IP 54
Ambient temperature	278 - 308 K (5 - 35°C)
Installation	wall mounting
Dimensions(with sampl.system)	700 wide x 1760 high x 375 mm deep
Weight	90 kg approx.

BRAN & LÜBBE

Analysentechnik

Industrial Analyzers

Environmental Monitoring

Information

B&L SENSIMETER G
Measuring System

AI 60.3 - 0480

B&L Gas Sampling System
for B&L SENSIMETER G - TUEV approved

Properly designed and mounted gas sampling systems are an indispensable prerequisite for reliable HF and HCl measurement.

When the sample temperature becomes lower than the dew point, a liquid phase is formed which absorbs strongly the polar HF and HCl molecules. Already at temperatures slightly above the dew point, there may occur adsorption to the surface which may result in major measuring errors, particularly in case of low concentrations. The same applies to the large-surface filter material. Consequently, the minimum sampling temperature is laid down acc. to the dew point. On the other hand, excessive temperatures will cause desorption from filtered dust particles and, consequently, measuring errors. Sampling temperatures of 160 - 200°C are proposed for waste gas monitoring.

The entire gas sampling system incl. sampling probe is heated, without any gaps. The sampling probe consists of stainless steel and the sampling line of PTFE. The rugged sampling system is conveniently accessible and simple to inspect and service.

General

The sampling point for the gas to be analyzed should be located at a point of the plant supplying representative concentration levels. Analyzers to be used acc. to the statutory requirements of the Clean Air Act must be installed in cooperation with an Agency determined by the Approval Authority. Several flue gas ducts may be connected to a single stack. Representative sampling is ensured after thorough mixing only. The mixing zone should be at least 3 stack diameters so that the sampling point must be located high enough above the ends of the gas ducts.

In the B&L Gas Sampling System, the sample is drawn through a sampling probe and passed through the sampling line to the B&L SENSIMETER G. The suction pump is mounted in the analyzer.

For using the measuring system in treated waste gases containing less than 150 mg dust/m^3, there are mounted quartz wool dust filters at the end of the sampling probe and at the analyzer inlet. For higher dust concentrations, a sintered metal frit may be attached to the tip of the probe.

The B&L Gas Sampling System for the B&L SENSIMETER G Measuring System is designed acc. to the properties of the sample. The heating ensures the necessary temperatures in the thermally insulated system.

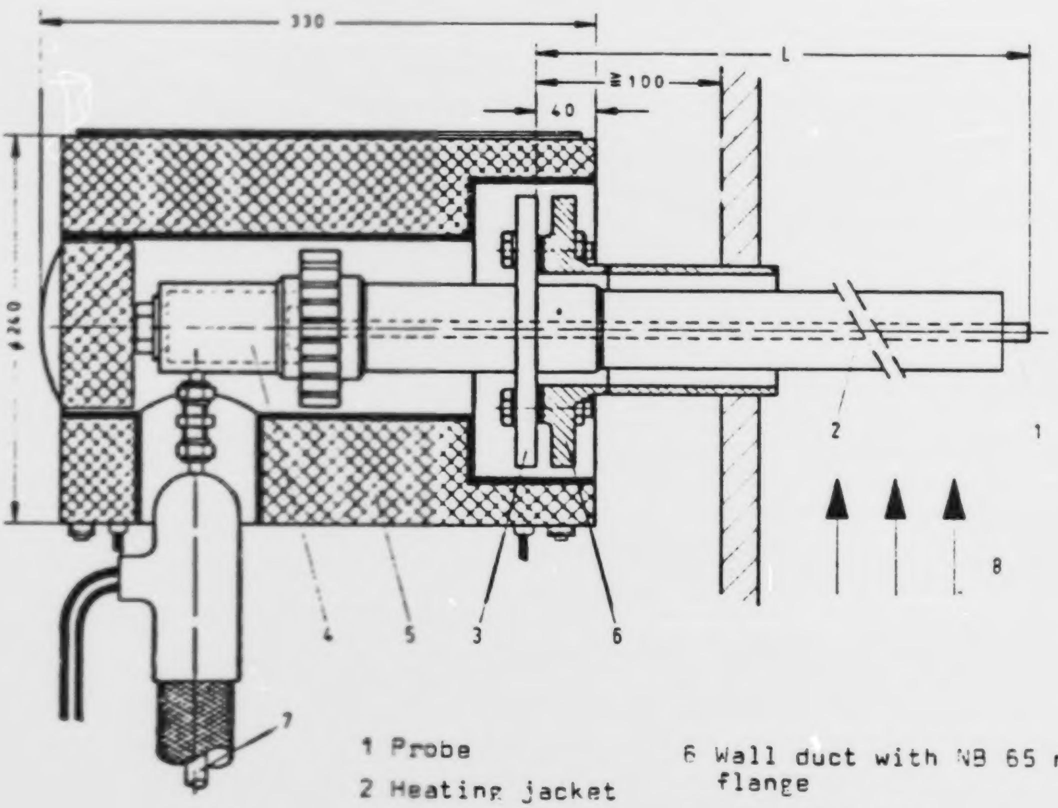
The gas sampling system comprises:

1. Sampling probe (electrically heated, with dust filter)
2. Sampling line (flexible, electrically heated, thermostat-controlled), length: 2, 3, 5, 10, 15, 20, 25, or 30 m. For longer distances, two or more lengths are connected by means of clamping ring joints. The max. length of the individual sampling line is 30 m, acceptable length total 120 m.
3. Connection to analyzer (electrically heated, with dust filter).
4. Power unit of the temperature control for the sampling system incorporated in the B&L SENSIMETER G.

Sampling probe

The gas sample should be drawn at right angles to the direction of flow. The probe must project about 1 m through the wall of the stack or duct, or to the centre of small-diameter stacks.

For installation, the user must provide a wall duct with NB 65 mm flange to DIN 2573, tube length acc. to local conditions.



1 Probe
2 Heating jacket
3 Flange NB 65 mm
4 Dust filter
5 Filter heating

6 Wall duct with NB 65 mm flange
7 Sampling line
8 Stack/waste gas system

L = mounting length

Sampling line

Gas sampling lines are available up to a max. length of 30 m. For longer distances, combine two or more lengths and heat by means of heating collars.

The sampling line consists of a heated flexible tube, min. permissible bending radius 200 mm. Padded, heat-resistant clamps must be used for fastening the sampling line to vertical walls.

Heating collars are at the ends of the sampling line. They can be mounted conveniently by means of quick-release fasteners or tension bands. The electrical supply and probe lines for the heated sampling probe and the heated collar of the probe head are in the heated sampling line so that for electrical connection only an ISO terminal box included in the supply must be mounted. All heating devices and temperature probes are connected to the power unit of the B&L SENSIMETER G.

Specs and data:

Sampling probe

Waste gas temperature	293 - 873 K (20 - 600°C)
Material	1.4571 stainless steel
Heating	electric, to about 480 K (200°C)
Dust filter	existing, heated
Length from flange	700; 1200; 1800 mm
Weight	20 kg approx.
Installation	user to provide wall duct with flange NB 65 mm to DIN 2573 or to DIN 2631
Position	horizontal

Accessories:

Sintered metal frit	required for dust loads exceeding 150 mg/Sm^3

Sampling line

LP flexible tube of plastic foam with PTFE core and protective stainless steel braiding.
Electric. heated (acc. to VDE Rules), moisture-proof.
Integral temperature probe (Pt 100).

Connections:	for B&L Sampling Probe and analyzer connection.
Heating collar:	for electr. heated dust filter at the analyzer

Power unit (incorporated in the B&L SENSIMETER G)

Power switch- fuses, and temperature controller for the electric heating system of the complete gas sampling system.

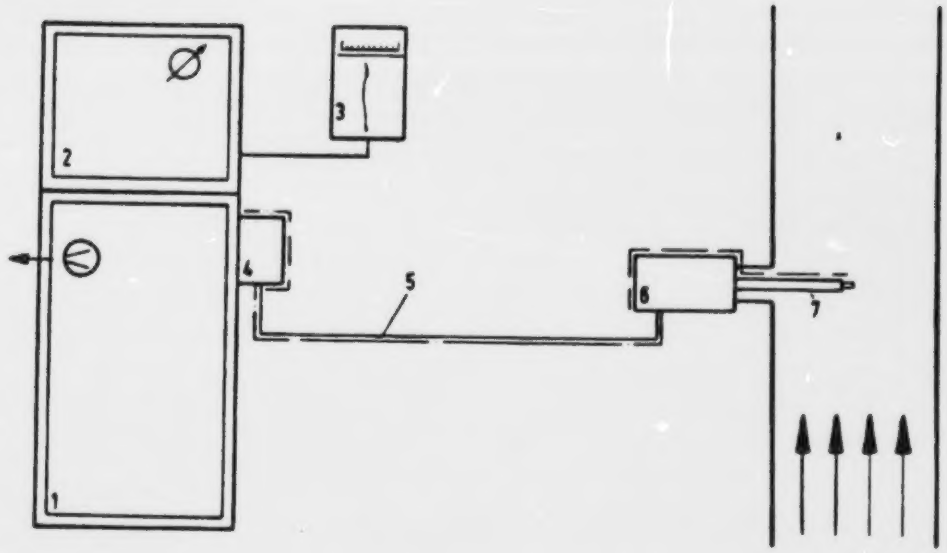
Power supply:	220 V, 60 Hz

Power consumption

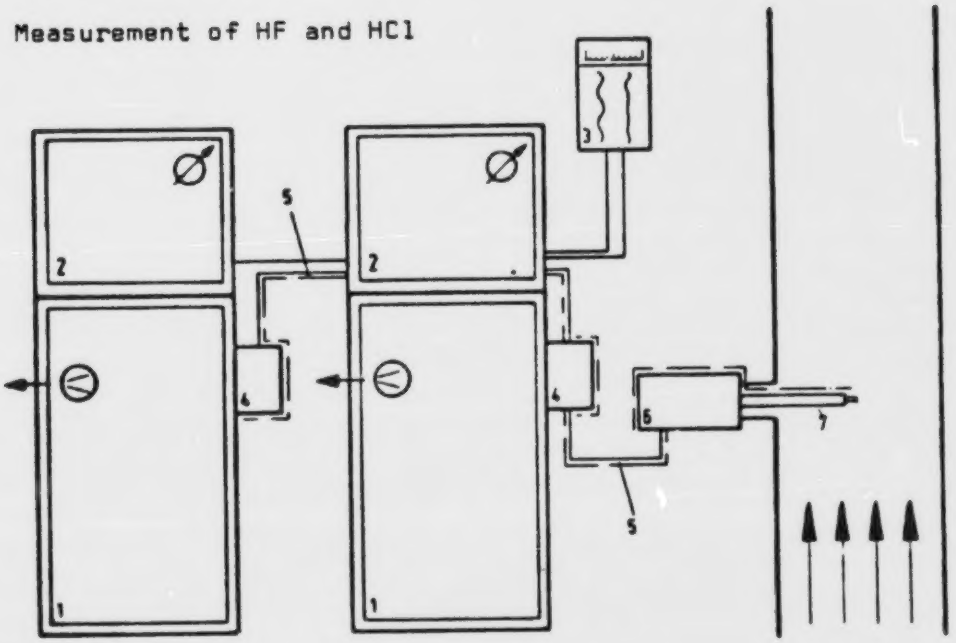
Sampling probe 1200 mm	600 VA approx.
Sampling line	130 VA approx. per m
Analyzer	70 VA approx.

B&L SENSIMETER G Measuring System

Measurement of HF or HCl

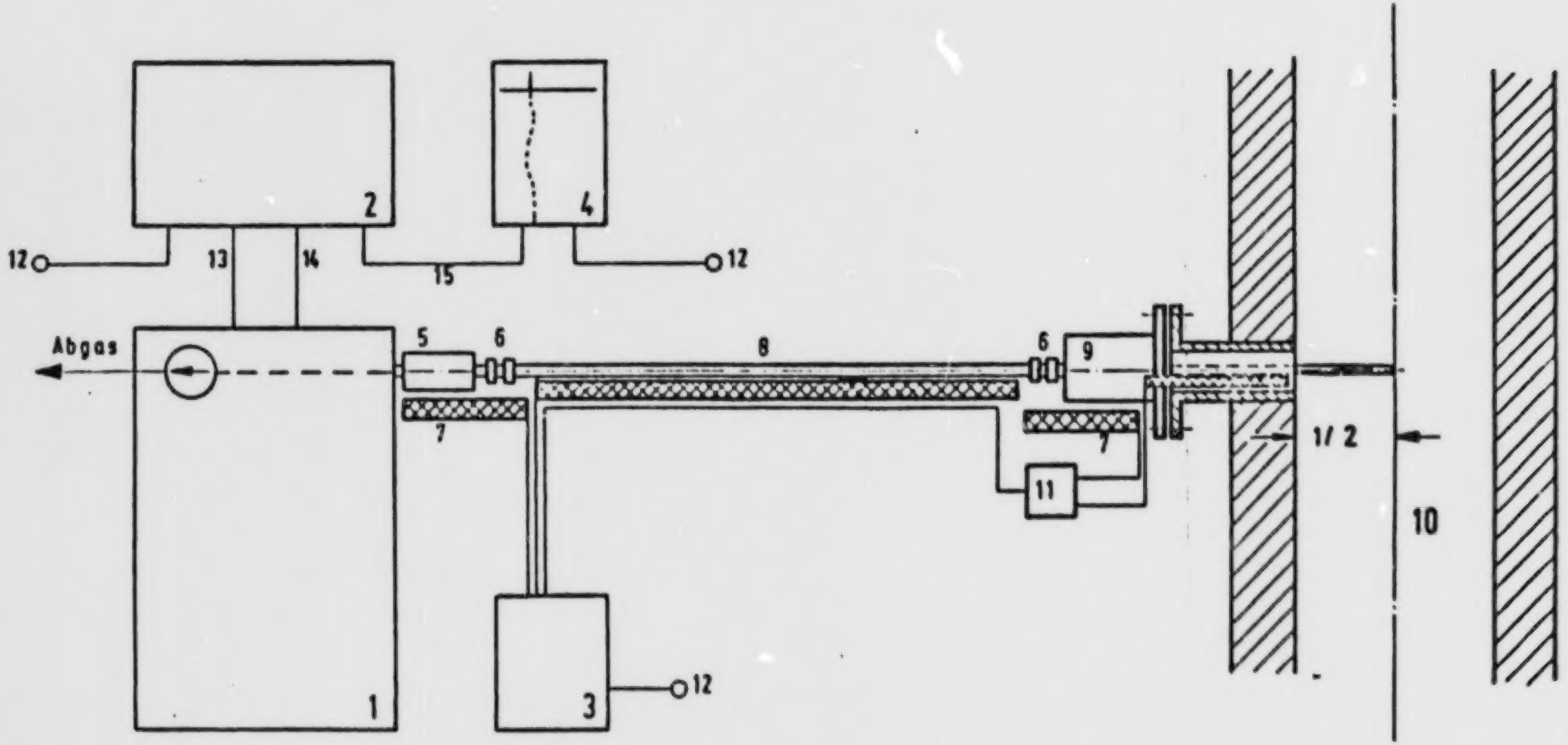


Measurement of HF and HCl



1 Analyzer unit
2 Control unit
3 Recorder
4 Dust filter (heated)
5 Sampling line (heated)
6 Dust filter (heated)
7 Sampling probe (heated)

Schema Rauch-und Abgasmeßanlage
SENSIMETER G

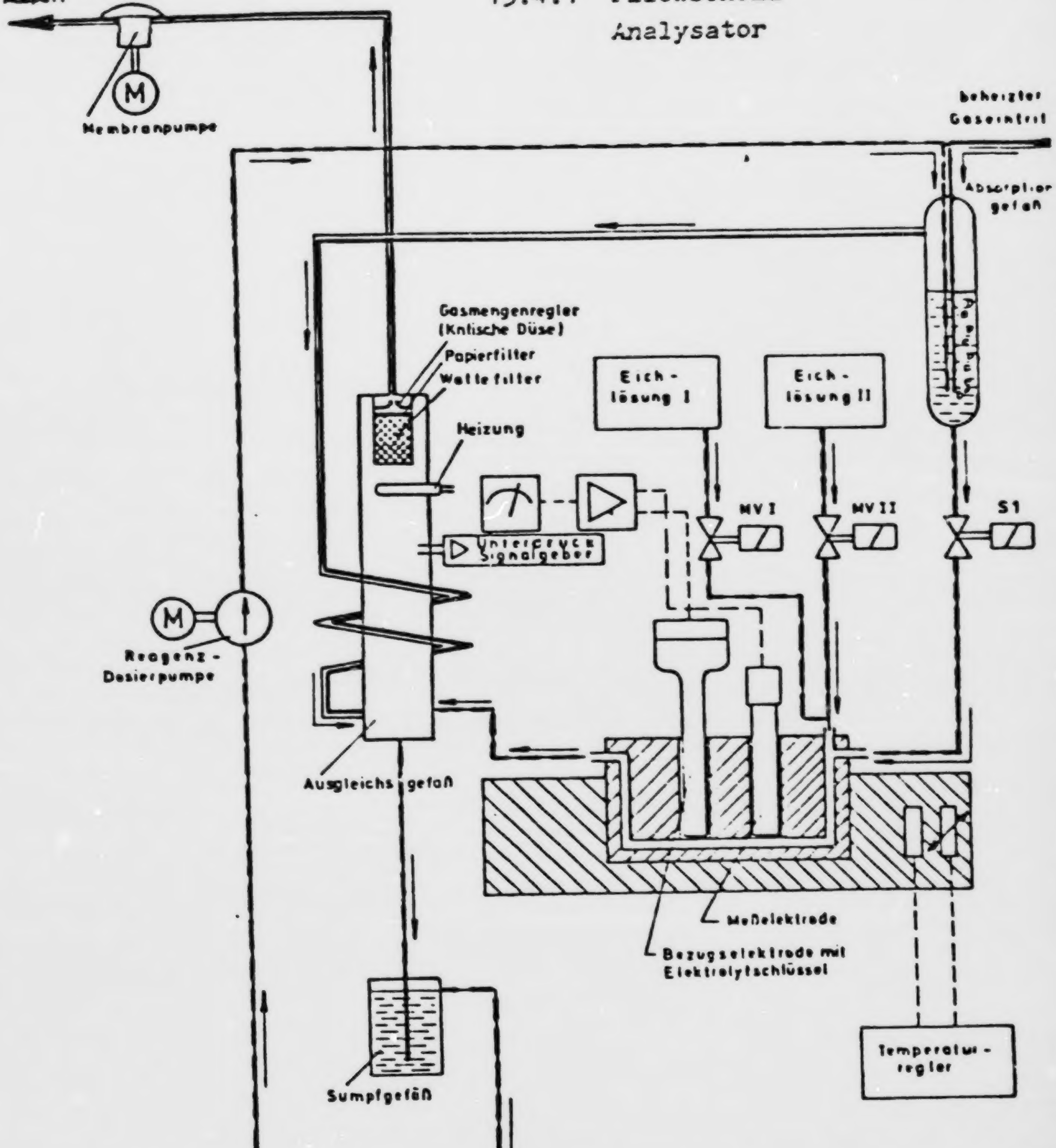


1 Analysator Sensimeter G
2 Steuerteil
3 Schaltschrank mit Temp. Regelung für Gasentnahmesystem
4 Registriergerät

6 Rohrverbinder 10 mm Ø
7 Heizmanschette
8 Probenahmeleitung (flexibel-beheizt)
9 Entnahmesonde (beheizt) mit Staubfilter

11 Klemmenkasten
12 Netzanschluß
13 Steuerleitung
14 Meßleitung
15 Meßsignal

13.4.1 Fließschema Analysator


Auspuff
M
Membranpumpe
beheizter Gaseintritt
Absorptionsgefäß
Gasmengenregler (Kritische Düse)
Papierfilter
Wattefilter
Heizung
Eichlösung I
Eichlösung II
MV I
MV II
S1
Unterdruck Signalgeber
M
Reagenz-Dosierpumpe
Ausgleichsgefäß
Meßelektrode
Bezugselektrode mit Elektrolytschlüssel
Sumpfgefäß
Temperaturregler
Reagenztank
Ablaufsammeltank
Gas
Reagenz
Ausgleichsleitungen

E-1900

BRAN & LUEBBE

Ontario Research
Mississauga
Ontario, Canada L5K1B3

Quotation

Quotation No. 53 089 428
(please state in all correspondence)

Your Ref.:
Date:

Date: 2.1.1985
Our Ref.: AP Ad/He
Dealt with by: Dipl.-Phys. Adomeit

Subject: HF-Monitoring Equipment B&L Sensimeter G

Subject to our General Conditions of Sale and Delivery and, recallable until confirmation of order, may we please quote as follows:

1 B&L Sensimeter G
a fully automatic industrial analyzer
for determining HF in stack gas

Measuring range	0.2 ... 20 mg/Sm^3
Signal output	0 ... 20 mA
Power supply	220 V ±10%, 50 Hz

Scope of supply as per Data Sheet
AI 61.3 E-0883

Price DM 49,630.--

1 B&L Gas Sampling System
for continuous waste gas sampling,
for monitoring HF
consisting of:

Sampling probe,
for installation in a stack or waste gas duct, about 1.2 m long, with electric heating and dust filter

- 2 -

Sampling line
(length as ordered)
flexible, with electric heater incl. temperature control, heating collars for the junctions at the sampling probe and the analyzer

Controls,
integrated in the Sensimeter-housing, with all required fuses, controllers and switches

Design and construction as per Data Sheet AI 60.3-o48o

Price of gas sampling system with	
sampling line 5 m long	DM 12,830.--
10 m long	DM 15,340.--
15 m long	DM 17,910.--

Optional:

For outdoor installation or rough environmental conditions:

1 Protective instrument cabinet
for accommodation Sensimeter G
dimensions: 214o mm high x 135o mm
wide x 135o mm deep
with walls, doors, and roof of glass-fibre reinforced polyester with PU foam core for insulation (sandwich design), grey to RAL 7032, one double door 2ooo x 125o mm

Price DM 10,770.--

1 Single-Pen Dot Recorder
with moving coil meter, calibrated acc. to range, with synchronous motor drive, in a standard housing for wall fastening, 144 mm x 144 mm

Price DM 2,080.--

1 Service box,
with recommended spares and wear parts for analyzer maintenance

Price DM 810.--

special packing DM 1,150.--

The prices quoted cover delivery fob Hamburg excluding installation and commissioning.

Three complete installation and operation manuals will be supplied for either unit on shipment. Extra copies are available at cost.

The quotation is based on the data, information, and specs at hand. Revisions and supplement due to new data and facts becoming known at a later date are reserved as are also design and technical modifications.

Our qualified instrument technicians, chemists, and engineers will be available for site discussions, commissioning, and operator training, at our usual erecting rates and conditions. Such services must be ordered not later than 4 weeks prior to the desired commissioning date, after performance by the user of all local preparatory works e.g., erection of equipment as well as provision of sampling lines and power supply.

In case of variation in our manufacturing cost we reserve the right to charge the price applicable at the date of shipment.

Time of Delivery: 5 months after receipt of order

Terms of Pyment: within 30 days from date of invoice

Guarantee:

The analyzer systems will be subjected to an extended shop running test for proper operation and measuring accuracy. Subject to compliance with our instructions for installation and operation, technically correct installation, and proper maintenance, guarantee is accepted for trouble-free and regular operation.

All parts becoming unserviceable within 12 months (8ooo operating hours) from commissioning, but not later than 24 months from shipment, due to poor material and/or faulty fabrication or shop assembly will be replaced by us free of charge by sending the necessary parts freight paid on carriage-paid receipt of the u.s. parts. The guarantee does not cover wear parts.

Bran & Luebbe GmbH
Analyzer Department.

Encl.
Terms and Conditions for Export-Deliveries

a/t/2o7

Number/
Numéro

4

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS -PHASE II

FINAL REPORT
PHASE B

DSS FILE NUMBER	26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER	0SQ83-00230
CANMET PROJECT NUMBER	410252

POLLUTECH LIMITED 1090 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1900

POLLUTECH

EFFECT ON THE ENERGY EFFICIENCY OF TUNNEL KILNS MANUFACTURING STRUCTURAL CLAY PRODUCTS OF FLUORIDE EMISSION CONTROL SYSTEMS
PHASE II

Final Report

Phase B

By

POLLUTECH LIMITED

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS FILE NUMBER : 26SQ.23440-3-9079
DSS CONTRACT SERIAL NUMBER : OSQ83-00230
CANMET PROJECT NUMBER : 410252
CANMET SCIENTIFIC AUTHORITY : Mr. K. Bell

96pp

March 31, 1985

OCT 11 1985

MICROMEDIA

POLLUTECH LIMITED 1090 SPEERS ROAD, OAKVILLE, ONT. L6L 2X4
TELEPHONE: (416) 844-1800

ACKNOWLEDGEMENT

ACKNOWLEDGEMENT

The Project Team consisting of staff from Pollutech Limited and the Ontario Research Foundation wish to gratefully acknowledge the assistance provided by the following brick companies, and their staff, in providing samples for analysis for fluoride content:

- Toronto Brick
- Brampton Brick
- Hamilton Brick
- Domtar Construction Material
- Canada Brick
- St. Lawrence Brick
- I-XL Industries
- Citadel Brick
- Clayburn Industries
- L.E. Shaw
- Estevan Brick
- Scott Brick
- Trinity Brick

We also wish to extend an additional thank you to the following plants, and staff, who provided detailed operating data on the production facilities, entertained our many questions during the site visits, and provided bricks and/or raw materials for detailed fluorine evaluation tests:

- I-XL Industries Limited
  Red River Brick & Tile Division
  Winnipeg, Manitoba
- I-XL Industries Limited
  Northwest Brick & Tile Division
  Edmonton, Alberta
- I-XL Industries Limited
  Redcliff Pressed Brick Division
  Redcliff, Alberta
- L.E. Shaw Limited
  Halifax, Nova Scotia
- Citadel Brick Ltd.
  Quebec City, Quebec
- Briqueterie St. Laurent
  LaPrairie, Quebec
- Domtar Construction Materials
  Ottawa, Ontario
- Domtar Construction Materials
  Mississauga, Ontario
- Canada Brick Co. Ltd.
  Streetsville, Ontario
- Canada Brick Co. Ltd.
  Mississauga, Ontario

POLLUTECH

PHASE II

PROJECT ABSTRACT

- PHASE A
- PHASE B

PHASE II

PROJECT ABSTRACT
PHASE A AND PHASE B

Pollutech Limited have conducted a technical investigation, using additional expertise from the Ontario Research Foundation, in which laboratory scale studies were used to examine means of inhibiting fluoride emissions from tunnel kilns and for brickmaking purposes. The procedures employed were aimed at providing possible alternatives to conventional emission control scrubbers since it was believed, as a result of the Phase I study, that scrubbers would upset thermal balances and result in energy inefficiencies.

The results of the technical investigations are reported separately for Phase A and Phase B of this study. The Phase A report refers specifically to the results of the fluoride analysis on raw materials utilized in Canadian brickmaking plants, the fluoride emission profiles of selected samples under simulated plant conditions, and the development of theorized optimized firing curves for each sample tested. The Phase B report deals with the results of a literature search and experimental program to examine the efficacy of additives and fluxes in inhibiting fluoride evolution from the selected samples.

The results of the **PHASE A** study indicated that:

- the analysis of fluoride in various raw materials from a broad sample of Canadian plants showed fluoride levels ranging from 202 ppm to 1163 ppm, with an average fluoride content of 706 ppm (0.07 percent)

- the variation in fluoride content of the raw materials was related to the geographical area from which the raw material was excavated

- the rate of evolution of fluoride from test brick samples was found to be directly related to the firing temperature, with the most significant fluoride loss at 800°C to 1000°C

- the rate of fluoride evolution varied significantly across the samples tested, ranging from 15 mg/kg-hr to 149 mg/kg-hr, depending on raw material utilized and specific brickmaking practices employed

- in most instances the rate of fluoride evolution is too high to be able to limit the release of fluoride by modification of the firing curve, unless significant reductions in kiln retention time (particularly at the soak temperature), and top firing temperature could be achieved

- gross energy calculations suggest the energy impact of changing the firing sequence is positive (i.e. savings) for those modifications that result in a decrease in fluoride evolution

The results of the **PHASE B** study showed that:

- a review of the literature suggested that a number of additives are available that may be used to limit fluoride evolution by complexing with the fluoride to limit fluoride release upon firing

- the literature also suggested that additives are available that can be added to the raw material, such that the physical properties of the raw material are modified, thereby limiting the release of fluoride

- laboratory testing using the various additives did not appear to have a significant effect on the handling of the raw material or the fabrication of the final product

- the use of additives to complex the fluoride did not result in a significant reduction in fluoride release during firing, and on some occasions fluoride emissions increased

- the use of additives to change the refractory characteristics did not result in a significant reduction in fluoride release during firing

The overall conclusion that can be drawn from the study is that procedures utilizing firing curve control in the **PHASE A** study cannot effectively be given serious consideration for fluoride emission control due to the high rates of fluoride emission and corresponding kiln retention times. The only way the fluoride loss can be decreased is by reducing the total amount of time the brick is exposed to the high temperatures (800°C-1000°C), by a reduction in firing time in conjunction with a reduction in the top firing temperature. This is unlikely to be a satisfactory solution to the problem however, since it would have deleterious effects upon the desired physical properties of the clay brick products so produced. The use of chemical additives in the **PHASE B** experimental program clearly demonstrates that this alternative does not have a great potential as a solution to fluoride emission control at Canadian brickmaking plants.

POLLUTECH

PHASE B - FINAL REPORT

- Literature Review on Additives and Fluxes
- Experimental Program to Evaluate Additives and Fluxes

PHASE B - FINAL REPORT

TABLE OF CONTENTS

Page No.

1. SUMMARY 1
2. PROJECT BACKGROUND 5
   - 2.1 Introduction to Problem 5
   - 2.2 Canadian Clay Brick Manufacturing 8
   - 2.3 Control of Fluoride Emissions By Modification of Raw Materials 11
3. TECHNICAL WORK PROGRAM 13
   - 3.1 Fluoride Suppression By Additives Which Change Brick Chemistry 13
     - 3.1.1 Literature Search 13
     - 3.1.2 Fluorine Chemistry - Properties of Fluoride Compounds 14
   - 3.2 Densification of Bricks to Reduce Fluoride Emissions 15
   - 3.3 Experimental Studies to Evaluate Additives 16
4. RESULTS OF TECHNICAL STUDY 19
   - 4.1 Literature Review on the Use of Additives for Chemical Suppression 19
   - 4.2 Evaluation of the Properties of Fluoride Compounds 22
   - 4.3 Literature Study on the Use of Additives for Densification 24
   - 4.4 Experimental Program on Chemical Additives 25
     - 4.4.1 Chemical Additives to Suppress Fluoride Evolution 25
     - 4.4.2 Chemical Additives for Brick Densification 26
     - 4.4.3 Porosity of Fixed Products 27
5. CONCLUSIONS & RECOMMENDATIONS 28

TABLES
FIGURES
APPENDICES

SUMMARY

1. SUMMARY

The second phase of this project was instituted to review the use of additives to raw materials to control fluoride evolution during the kiln firing process through an examination of the existing literature, and thereafter by way of experimental tests.

In order to minimize fluoride emissions the raw materials should be selected from either sources low in fluorine content or from sources which exhibit slow rates of fluoride evolution during firing. However, since the supply of brickmaking clays and shales is somewhat limited in Canada and since companies would prefer to use those captive deposits already available, modification of the raw material to limit fluoride evolution by means of additives was considered worthy of a preliminary study. The use of such materials as calcium hydroxide to capture the fluorine and/or ceramic fluxes to reduce firing temperatures and reduce porosity at lower temperatures has been suggested as viable means of achieving these ends. In addition the incorporation of additives to change the particle packing during extrusion forming (such as deflocculants) is equally viable and has been assessed here.

The Phase B program was divided into three sub-sections in order to examine the efficiency of additives and fluxes in inhibiting evolution from selected clay and shale samples. The tasks carried out to complete this phase were as follows:

- Literature Review

  Although literature reviews on the chemistry of fluoride evolution and control mechanisms using conventional scrubber technology was available, there was little information readily accessible on the topics of ceramic fluxes and their combined effect upon firing temperature microstructure development, and fluoride evolution, or on the topic of additive use for immobilization or capture of fluorine in situ. Therefore a literature survey on these topics using a CANOLE computer searching facility was conducted to evaluate current scientific literature on the feasibility of controlling fluoride emissions by such techniques.

- Development of an Experimental Program to Study Reduction of Fluoride Emission

Based upon the results of the literature review, and in consultation with the Scientific Authority, a series of potential additives were selected for incorporation with typical brick making raw materials. Twenty variations were examined which were aimed at inhibiting fluorine evolution by either fluorine capture, fluxing of the clays to reduce firing temperature, or porosity reduction in the extruded products.

- Experimental Evaluation of Fluoride Release

Twenty compositional variations on four preselected typical raw materials (i.e. total of 20 samples plus blanks) were prepared for fluoride evolution analysis. Samples were batched in typical ceramic mixing equipment and extruded into cylinders for firing. All samples were fired according to the actual plant firing schedules provided by the relevant manufacturer. The macrostructure and microstructure of the fired extruded bars were subsequently evaluated to determine porosity levels as manufactured.

Fluoride evolution from the fired samples was assessed by measurement of fluoride content before and after firing using the analytical technique detailed in the Phase A report. All results were compared with data obtained previously for untreated naturally occurring raw material.

In order to complete all of the tasks as outlined, the project team undertook the following steps:

- a key word search was prepared to identify what selections would be reviewed in the computer literature search
- a computerized literature search was carried out on the CANOLE system, searching the data basis for Chemical Abstracts, National Technical Information Service (NTIS), and Enviroline
- 25 technical abstracts, out of a total 420 selected titles, were reviewed in detail for the evaluation of the use of addition for densification
- 7 chemical additives with four selected raw materials were evaluated experimentally by preparation of extruded samples, firing according to actual plant schedules, and porosity (microstructure) analysis
- fluoride analysis was completed on fired samples, with and without additives, to determine any change in fluoride release caused by the additives

Completion of all of these tasks in Phase B provided a clear indication of the feasibility of using additives to control fluoride evolution by modification of the chemical structures. Specific inferences from this work are as follows:

- a number of additives are suggested by the literature that could be used to limit fluoride evolution, by complexing with the fluoride to limit release upon firing, or that can be added to the raw material, such that the physical properties of the product are modified, thereby limiting the release of fluoride

- laboratory testing using the various additives did not have a significant effect on the handling of the raw material or the final product

- other than for one sample, the use of additives to complex or trap the fluoride did not result in a significant reduction in fluoride release during firing

PROJECT BACKGROUND

- Introduction to Problem
- Canadian Clay Brick Manufacturing
- Control of Fluoride Emissions By Modification of Raw Materials

2. PROJECT BACKGROUND

2.1 Introduction To Problem

While the clay brick manufacturing industry is not generally recognized as a major source of industrial pollution, it has been identified as a significant source of gaseous (and occasionally particulate) fluorides. The fluoride emissions are generated by the action of heat, during the kiln firing process, on fluoride and fluorosilicate minerals closely associated with the clay and shale raw materials used in brick manufacturing.

It is well known that the emission of gaseous and particulate fluoride compounds from industrial sources can present some hazard to the environment by:

- endangering the health of agricultural and foraging animals (and in extreme cases, the health of humans)
- causing damage to vegetation (foliage)
- contributing in general to acid rain

Concern has recently been expressed by the various regulatory agencies over fluoride emissions and it is anticipated that if these agencies seek to control such emissions, some Canadian clay brick manufacturers will be required to reduce the evolution of fluoride compounds from their plants.

The kiln firing operation, which is the major production rate determining operation in the total clay brick manufacturing process, is also the major energy cost source in clay brick manufacturing. Most plants operate on a continuous basis using tunnel kilns which burn fossil fuels. Since the rapid escalation in the cost of oil and gas in the early 1970's, the Canadian clay brick industry has actively worked towards the optimization of its kiln firing operation in order to minimize energy consumption within the manufacturing process. It has been noted that between 1972 and 1981, energy consumption per manufactured unit, within the industry, has decreased by nearly 29 percent. The improvement in efficiency has been obtained by carefully balancing burner operation, load movement through the kiln, air movement through the kiln, and recirculation of both hot combustion gases and cold air to give optimum product quality and minimum fuel usage. Due to the delicate balance and control which has been developed, and is now required to ensure the energy efficient operation of dynamic systems such as tunnel kilns, it is anticipated that the incorporation of conventional emission control measures such as scrubbers could result in a serious reduction of the kiln energy efficiencies achieved in recent years. A major loss in energy efficiency would seriously hamper the industry's ability to compete with other construction materials in the marketplace.

It is essential, therefore, that any measures employed to reduce or control atmospheric emissions are selected on the basis of their possible impact on energy efficiency in addition to their efficacy and reliability as anti-pollution devices. In principle, control of fluoride emissions from tunnel kilns, used for manufacturing clay bricks, can be applied at one of the following three stages in the brickmaking process:

- During selection of raw materials - i.e. select raw materials with a potential for reduced fluoride emission and/or incorporate additives to suppress fluoride evolution.

- During kiln firing process - i.e. alteration of the firing procedure to reduce the rate of fluoride evolution.

- At the gas exhaust stack - i.e. by incorporation of conventional scrubber systems (wet or dry).

The results of the Phase I study by the Clay Brick Association which evaluated installations in Germany suggested that flue gas cleaning systems using conventional wet scrubber technology should only be considered as a last resort due to both major capital operating and running costs, and unreliable performance. A preventative approach through raw material alteration and modification and/or the implementation of changes in the firing process to reduce fluoride evolution at its source appear to be the better alternatives, and therefore the purpose of this study.

Fluoride evolution and fluoride emission control procedures as they relate to the clay brick manufacturing process have been studied in great detail in Europe, particularly in West Germany, and it is clear from published literature that alternative techniques which utilize raw material modification and/or alteration of the firing process are potentially available. Not all European scientists however, agree with this approach.

It is recognized that Canadian manufacturing and kiln-firing technology together with Canadian raw materials differ significantly from those used in Europe. The introduction of these European approaches to North America require significant research on the interrelationship of the thermochemistry of fluoride evolution from Canadian clays and shales with known kiln firing technology and current standard practice. The object of this study was, therefore, to develop guidelines to assist the clay brick industry in selecting energy efficient fluoride control methodology.

2.2 Canadian Clay Brick Manufacturing

The Canadian Clay Brick Industry is made up of thirteen companies operating twenty-three manufacturing plants across the country from Newfoundland to British Columbia. In recent years these companies have collectively manufactured and/or sold in excess of 600 million brick equivalents per year. Typically, the brick making process requires an energy consumption of approximately 5.5 GJ per thousand brick equivalents (5.2×10^6 BTU per thousand brick equivalents).

The manufacturing process for structural clay products typically comprises the following major activities:

- Excavation of raw material - local clays and shales.
- Crushing and grinding to the desired particle size distribution.
- Addition of modifying ingredients - e.g. pigments, barium carbonate for scum control, plasticizers and/or binders.
- Conditioning/tempering with water to produce a suitably plastic mass.
- Forming - by high pressure continuous extrusion through dies of the desired cross-section, followed by cutting to the required size.
- Loading onto kiln cars.
- Drying (in tunnel dryers).
- Firing (in continuous tunnel kilns).
- Unloading, grading, packaging and shipment.

As an impurity in clays and shales, fluorides are widespread. Because fluoride and hydroxyl ions are of nearly equal size and both are monovalent, isomorphous substitution of one for the other can be anticipated in clay mineral structures. In addition, these raw materials also contain many other hydroxyl bearing accessory minerals such as mica, hornblende and apatite, among others, all of which are known to contain strongly-bound fluorine.(1) Coupled with the frequent presence of the mineral fluorspar (CaF_2), these sources provide a potential for fluoride emissions during the ceramic firing cycle.

During the heating stages of the ceramic manufacturing process, the fluoride present in the raw materials is primarily evolved as gaseous hydrogen fluoride (HF) or silicon tetrafluoride (SiF_4), although particulate calcium fluoride (CaF_2) and particulate ammonium fluosilicate(2) $(NH_4)_2SiF_6$ may also be formed when organic impurities are present.

Early estimates of the contribution of the brick industry to the total industrial fluoride emissions were based entirely on laboratory experiments and assumed that all of the available fluoride in the clay or shale was evolved. It has been clearly demonstrated in recent years (3,4) that only a portion of the available fluoride is in fact emitted during the firing operation.

The relative proportion of fluoride evolved is obviously not the same for every clay fired to the same temperature;(1) it will vary with each raw material and with differences in equipment and operational procedures from plant to plant. Fluoride emission occurs during the firing process when the fluorine compounds entrained within the body become thermodynamically unstable. While the presence of water vapour trapped within the firing atmosphere appears to be of prime importance, there are several other important controlling factors, namely: (3,4,5,6,7)

- Firing Cycle- The total firing time, the maximum firing temperature and the dwell time between 800°C and the sintering range of the clay.

- Type of Kiln- Tunnel kilns can be expected to be the source of higher emissions than periodic kilns. The high rate of flow of flue gases, air and humidity over the ware at elevated temperatures increases the rate of removal of fluoride. For example, products in the centre of the kiln charge (hack) will lose less fluoride than those on the outer edges of the kiln car due to temperature gradients and less exposure to high velocity gases.

- Kiln Operating Conditions- The kiln atmosphere, air/fuel ratios, type of fuel, air leakage and the degree of gaseous recirculation will influence the rate and extent of fluoride emissions during firing. Passage of hot gases (by recirculation) over the cooled charge may lead to readsorption of a portion of the evolved fluoride.

- The Degree of Compaction of the Product and Particle Size of the Raw Materials- Denser compacts have been shown to evolve less fluoride than less dense or more porous products. Similarly, finely-ground raw materials yield higher fluoride levels than dense coarse-grained materials. The cross-sectional dimensions of the ware will also influence fluoride emissions.

- Microstructure and Porosity of Product being Fired - Fluoride migration encounters little resistance in porous ceramic materials whereas the presence of densified phases can effectively impede diffusion.

- The Initial Fluoride Content of the Raw Material- Although fluoride emission is not in general stoichiometric, it may be presumed, other conditions being equal, that raw materials high in fluoride content will cause higher levels of emission.

- Calcium Carbonate Content - The presence of finely-divided, naturally occurring $CaCO_3$ in the raw materials has been cited as a factor in limiting the level of fluoride evolution (8).

2.3 Control of Fluoride Emissions By Modification of Raw Materials

The application of fluoride control technology by the modification of raw materials can be performed by the following different routes:

- the use of clays and shales with minimal fluoride concentrations;
- the removal of fluorine bearing minerals from the clays and shales, and
- the incorporation of some ingredient into the raw material mix which will suppress fluoride evolution during firing.

The first of these options is largely impractical in Canada because of a limited supply of brickmaking clays, especially in the more densely populated areas where the demand for bricks is high. The second option, beneficiation to remove fluoride, is probably technically feasible using flotation and other mineral dressing techniques, however, such an approach is undesirable from materials handling or economic standpoints. The third option, the formulation of the brick to suppress fluoride is the simplest approach and probably shows the most potential for reducing fluoride emissions. It would be a straightforward matter to make slight changes in the green brick composition. The investigation of this third option is the subject of the Phase B report.

During the Phase B program the study team investigated brick raw material selection such that ingredients which would suppress fluoride evolution during firing were incorporated into the raw material mix. This suppression could be by either a chemical or a physical mechanism. In the case of chemical suppression, a chemical or chemicals, which react with the gaseous fluoride were incorporated. When the fluoride was evolved from the clay matrix it was theorized that it would react with the chemical(s) to form a stable solid before the fluoride could migrate through the pores in the brick to the brick surface. In the case of physical suppression, ingredients which permit the formation of a denser unfired brick were incorporated into the raw material mix. In theory, when the fluoride was evolved from the clay matrix, its progress to the brick surface (and subsequent evolution) would be arrested by the dense, closed pore structure of the brick.

TECHNICAL WORK PROGRAM

- Fluoride Suppression By Additives Which Change Brick Chemistry
- Densification of Bricks to Reduce Fluoride Emissions
- Experimental Studies to Evaluate Additives

3. TECHNICAL WORK PROGRAM

3.1 Fluoride Suppression by Additives Which Change Brick Chemistry

To suppress fluoride emissions by chemical means, an admixture which reacts with gaseous fluoride could be incorporated into the raw material mix. When the fluoride evolves from the clay matrix it may or may not react with chemicals in the admixture to form a stable solid. There are two steps to take when investigating potential admixtures:

- a search of the literature to obtain published information

- a study of the chemistry of fluoride compounds to identify those which are stable at high temperatures.

Both of these steps were undertaken in the course of this study.

3.1.1 Literature Search

The literature search was performed using the computerized facilities at the Ontario Research Foundation. Three data bases, Chemical Abstracts (1967 -present), NTIS (1964 - present), and Enviroline (1970 - present) were searched. The search profile employed was as follows:

Set	Description
1	Fluorine
2	Fluoride
3	1 & 2
4	Fixation
5	Immobilization
6	Entrapment
7	Stabilization

Set	Description
8*	3 intersect 4
9*	3 intersect 5
10*	3 intersect 6
11*	3 intersect 7
12	Clay
13	Brick
14*	3 intersect 12
15*	3 intersect 13

All items in sets marked with an asterisk (*) were printed offline.

A total of 420 titles were printed, the majority (approximately 95%) from Chemical Abstracts. From these 420 titles, 95 were considered potentially relevant and abstracts were obtained. After this final screening, 25 of the abstracts were considered relevant. Many of these abstracts were from foreign language publications, and in most cases it was felt that obtaining the actual publication was a time-consuming, expensive task which would yield little more information than that in the abstract. Thus in many of the cases, much of the information relayed here was obtained from the abstract.

3.1.2 Fluorine Chemistry - Properties of Fluoride Compounds

A second method of investigating potential clay additives to reduce fluoride emissions is the study of the properties of fluoride containing compounds. Fluoride is extremely reactive and forms compounds with about 64 of the other elements in the periodic table. (This doesn't include organo fluorides including ammonium salts.) Obviously, it would not be feasible to form many of these compounds within the clay matrix because of instability at high temperature, toxicity and radioactivity. Furthermore, because it is not clear if the fluoride emitted during brick firing is present as F^- or as more complex ions such as AlF_5^{2-} or SiF_6^{2-}, compounds containing all three ionic forms must be included.

For the purposes of completeness, the physical properties of all the inorganic fluorine containing compounds listed in the CRC Handbook of Chemistry and Physics were obtained. The physical properties of the compounds are given in Table 1. The criteria on which each compound were judged are as follows:

- melting point greater than 1200°C
- low toxicity
- non-radioactive

3.2 Densification of Bricks to Reduce Fluoride Emissions

A potential alternative to the incorporation of admixtures to reduce fluoride emissions is the densification of the green brick. The theory is that when the gaseous fluoride is evolved, it diffuses through the open pore structure of the brick to the brick surface. If the brick porosity is reduced, the fluoride diffusion will be stopped at some point in the brick interior.

Methods of reducing brick porosity were investigated by conducting a literature search of the same indices searched in the first part of the study. The search profile was as follows:

Set	Description
1	Densification
2	Deflocculation
3	1 + 2
4	Ceramics
5	Bricks
6	Clay
7	4 + 5 + 6
8	3 Intersect 7

3.3 Experimental Studies to Evaluate Additives

In conjunction with the Scientific Authority 7 additives were selected on the basis of the literature reviews, to be evaluated in four different raw materials utilized for Canadian brick manufacturing. The details on which products were selected and how the experimental programs were implemented are outlined separately for chemical supression and densification. With respect to the shale samples from Area 1 and Area 6 (as discussed in the Phase A final report), the additives were Cerium Oxide, Strontium Carbonate, Barium Carbonate, Calcium Carbonate and Hydroxide, and a Lignosulfonate. The first five additives would reduce fluoride emissions through formation of fluoride compounds, whereas the lignosulfonate would reduce emissions by decreasing brick porosity. For the clay samples from Areas 2, 3, and 4, the additives were Calcium Carbonate and Calcium Hydroxide, Magnesium Carbonate, Strontium Carbonate and a combination of Sodium Carbonate and Sodium Silicate deflocculant. As above, the Calcium, Magnesium and Strontium additives would act by forming stable fluoride compounds, while the Sodium Carbonate and Sodium Silicate combination would act by decreasing brick porosity. In the case of the Cerium Oxide and the alkaline metal carbonates, the materials were added in finely divided (300 mesh) form.

The only reference in the literature regarding additive concentrations is one which suggests 50% stoichiometric excess of the metal ion and one which stipulates that Calcium Oxide concentration should be no greater than 5%. In the experimental portion of this program, a three-fold stoichiometric excess of the metal ion was added.

In the case of the deflocculants, a deflocculation curve using the specific clay and deflocculant to be tested was first obtained. From these deflocculation curves, the additive concentration was determined to be a point significantly progressed down the curve but not at the minimum point (i.e. lowest viscosity or highest fluidity). This position was adopted to aid in control of the extrusion operation and to prevent maximum packing from occurring in the extrusion column, which would probably cause machine damage. The deflocculation curves of the four raw materials with the relevant deflocculants are given in Figure 1.

For each experimental test run a 6 kg batch of clay/shale - additive mixture was prepared for extrusion. Details of each batch are given in Table 2. The alkaline metal carbonate materials and cerium oxide additives were initially dry blended with the respective clay or shale in a twin shell (V blender) for 1 hour. The mixture was subsequently mixed with water in a laboratory sized concrete mixer to ensure even dispersion of the water and finally passed twice through the extruder with no vacuum to ensure complete mixing (the extruded product was shredded before refeeding into the extrusion machine).

The calcium hydroxide addition was made in the form of a milk of lime slurry and was added directly into the wet mixing stage of the operation with the water addition. The deflocculants used were added in a similar manner by dispersing initially in the additive water fraction of the mix.

Because Sample #105 as received had a moisture content of 19%, further addition of water was not necessary. To incorporate the additives into the clay, 1 kg lots of the material were placed in a roller mixer. The appropriate amount of additive was mixed with a small amount of water and sprayed onto the clay. Several passes were made through the mixer to ensure thorough distribution.

Moisture contents of the extrusion mixes were maintained as close as possible to production data obtained from the field visits, consistent with the power limitations and smooth operation of the extrusion machine used. The moist material was then extruded through an auger type, de-airing extruder (under a vacuum of 24-25 inches of mercury) into 5.0 cm diameter cylinders. The extruded cylinders were cut to 6-8 cm sample lengths for firing. During the extrusion process, the power requirement of the extrusion machine was constantly monitored to ensure consistent products and if major variations occurred, the run was aborted and fresh batches were prepared and extruded.

The samples were covered with a towel to reduce the rate of drying (to prevent cracking) for a minimum of 72 hours. They were then oven dried (100°C) for 24 hours to complete the drying process.

The firing operation was conducted in a 5 KVA muffle furnace with interior dimensions 50 cm x 23 cm x 19 cm (l x w x h). Two thermocouples (B) were placed in the furnace as illustrated by Figure 2. The rear thermocouple was connected to a Datatrac multiloop temperature and power programmer/controller.

The temperature profiles obtained from the brick plants were entered into the controller to simulate the production firing of bricks in the laboratory muffle furnace. For each clay/shale sample, the firing curve provided by the associated brick plant was used. Thermocouple B was the controlling thermocouple whereas Thermocouple A which was close to the samples monitored temperatures actually achieved. The two thermocouples were connected to a strip chart recorder to provide a firing record. A trial run with the furnace empty showed Thermocouple A to measure a slightly lower temperature than Thermocouple B. Five samples from each batch were fired according to the desired profile. All the runs are given in Appendix 2. After firing the samples were ground and riffled to provide representative samples for fluoride analysis using the pyrohydrolysis technique.

In addition, samples of each fired product were retained for evaluation of porosity and pore size distribution as measured in a Micromeritics Mercury Intrusion Porosimeter. It was considered that any major variations in pore size distribution caused by the use of the aforementioned additives would be readily detected by this technique and may be related to anomalies or trends observed in the fluoride evolution measurements.

RESULTS OF TECHNICAL STUDY

- Literature Review on the Use of Additives For Chemical Suppression
- Evaluation of the Properties of Fluoride Compounds
- Literature Study on the Use of Additives for Densification
- Experimental Program on Chemical Additives

4. RESULTS OF TECHNICAL STUDY

4.1 Literature Review on the Use of Additives for Chemical Suppression

The literature search indicated that the most emphasis to date has been placed on the use of calcium added as lime (CaO) or limestone ($CaCO_3$) to reduce fluoride emissions by reaction to yield CaF_2. Each of the studies which has indicated a reduction in fluoride emissions will be discussed before presentation of contrary evidence.

In a review with 53 references, Graetz(9) indicates that CaO and MgO additions to the raw materials binds fluoride. Kolkmeier(10) also in a review, states that lime additives reduce fluoride emissions, particularly in low-lime clays. This positive influence, however, is not the case for lime-rich clays because the lime content of the raw material is sufficient to react with generated fluoride, and added lime may actually have a deleterious effect by resulting in higher porosity of the ceramic body. This view is supported by Mazzali et al(11) who state that at 900°C fluoride release is inversely proportional to the alkaline earth content of the raw materials and that the release can be lowered slightly by the addition of less than or equal to 5 weight percent CaO.

Handl(12) states that adding greater than a 50 percent stoichiometric excess of CaO (for example 1.5 percent CaO to a mixture containing clay with a fluoride content of 0.9 percent) results in 94% retention of the fluoride. Further support is provided by Bergmann & Troyer(13) who conducted a two-year study of fluoride emissions from 2 clay brick plants. They concluded that a higher CaO content in the feed of one plant (10.17 vs. 1.22 weight percent) resulted in reduced fluoride emissions (19 vs. 45 mg/m^3). The solid fluoride complex formed was $Ca_3Si_2O_7.CaF_2$. Also in this study no relationship between fuel sulphur content and fluoride emission levels was observed.

In a patent issued to Isake and Lazik(14) the sediment from $CaCO_3$ washing is mixed at a concentration of 6.5 weight percent (on a dry basis) in clay bricks. This treatment resulted in a fluoride emission reduction of 37%. In another patent, Haessler(15) describes the coating of ceramic pieces with a stoichiometric amount of a calcium compound. The fluoride emitted reacts with the calcium and remains on the ceramic piece.

Tuenker(16) describes studies on reducing fluoride emissions and states that limestone addition delayed emissions.

In related work, Koelling(17, 18) has studied the reduction of fluoride emissions from the thermal decomposition of phosphogypsum. The phosphogypsum contained 0.5% fluoride. It is indicated that pH is an important factor, thus residual phosphoric acid in the phosphogypsum promotes fluoride loss and that neutralization with lime reduces the fluoride emissions. The kiln temperature was 1250°C and 95% of the fluoride was retained in the product.

Work has also been performed with other chemicals. For instance absorption of gaseous fluoride by manganese ore was reported by Goncharenko et al.(19) A capture efficiency of 95.97% is reported. The temperature of the reaction is not reported, however the absorbent may be effective as an additive to the clay (as opposed to use on gaseous fluoride).

Kolkmeier(20) describes reduction in fluoride emissions using by-product metal hydroxides. It should be noted, however, that in such a case, quality assurance of the additive would be an important factor.

Two publications which discussed in more general terms the chemistry of gaseous fluoride were found. Schmidt(21) studied sulphur/fluoride interactions in ceramic kilns and stated that a high sulphur content promotes fluoride emissions because calcium will preferentially bind with SO_2, not fluoride, and the fluoride will be released. Byer et al(22) have published a paper regarding lime/fluoride reaction kinetics. Unfortunately, only temperatures up to 800°C were used as the reaction conditions; however, it was found that below 790°C the reaction product between lime and used potlining material from aluminum manufacture is CaF_2, but that above 790°C a eutectic complex, CaF_2CaSiO_4, is formed.

Finally, two papers have been published with views in opposition to those reported above. Bergmann(13) states the fluoride emissions were independent of fuel sulphur content in his studies, and Routschka and Majdic(23) state that lime did not reduce fluoride emissions in their experiments, and that CaF_2 itself decomposes at 1100°C. Only when the CaF_2 is well sealed from the kiln atmosphere will it not decompose at high temperatures.

To summarize, the information obtained from the literature on the use of clay additives to reduce fluoride emissions is not extensive but does clearly suggest the following:

- the effect of addition of alkali earth metals in the clay on fluoride emissions is not clear. It could be that other parameters such as lime concentration and particle size, firing profile, brick porosity, and fuel and clay sulphur content influence the reactions resulting in contradictory results being obtained by different laboratories

- it is not clear whether the gaseous fluoride exists as F^- or as other complex ions such as SiF_6^{2-} and AlF_5^{2-}. Furthermore, the form of the gaseous fluoride may depend on the original fluoride in the clay and the temperature at which it is liberated

- other additives (in addition to lime) which may be effective are manganese ore and waste metal hydroxides

4.2 Evaluation of the Properties of Fluoride Compounds

Of all the compounds listed in Table 1, only 16 pass the melting point test. All of these are the fluorine salts of divalent or trivalent metals ions. In many cases, the melting points of the hexafluorsilicate salts of these metal ions were not given and in no cases were the pentafluoraluminate salts of metal ions even listed. It is known that the pentafluoraluminate ion does exist as a calcium salt, having been identified in work by Frazier et al(24) on phosphogypsum. Information on its physical properties (including high temperature stability) was not found. In the cases where the melting points of hexafluorsilicate salts are given, the salts tend to decompose at much lower temperatures than the fluoride salts. Thus, if the fluoride is emitted from the clay matrix as the hexafluorsilicate or pentafluoraluminate ions, its immobilization may be a more complicated reaction than a simple anion displacement, i.e. the complex fluoro ion may decompose, producing a solid silica/alumina phase and gaseous fluoride which will subsequently react with the immobilizing metal. A detailed investigation into the chemistry of high temperature reactions which may occur in such systems was beyond the scope of this project. Therefore, it was assumed that the only metal ions which have the potential of reducing fluoride compounds are those which form high temperature stable fluoride compounds. If it is deemed that certain of these metal ions may be suitable from availability and toxicity standpoints, their actual effectiveness as fluoride suppressants will be determined empirically.

As mentioned previously, only sixteen fluoride salts which are stable at temperatures greater than 1200°C were found. For the most part, all of them are also toxic, however, other salts of these metals are not toxic, indicating that the toxicity is due to the fluoride ion, not the metal ion. Because the metals will be added as other salts, the toxicity aspect will likely not be a problem. The physical properties of other salts of these metal atoms, as well as their availability, were investigated, details being given in Table 3 and 4. Any salts that could potentially produce environmentally unacceptable by-products at high temperature, for example halides, nitrates/ites, and sulphates/ites, were not included as potential additives. In addition, many organo salts of the metals are also available, these were not listed because of their large number, but should be kept in mind as possible alternatives. The majority of these salts are low melting, i.e. at the high temperatures encountered in a brick kiln, the organic portion is probably oxidized and released as CO_2 and water vapour leaving the metal oxide behind. Because fluorine emissions increase with an increase in water vapour partial pressure, any substance which increases the humidity within the brick should likely be avoided. With this possible drawback in mind, the organo salts of the metals will not be the most promising additives and will be considered only if the other salts prove unsuitable.

Another consideration in the reformulation of brick raw materials is the form in which the additives can be included in the mix. For instance, if a compound is either:

- readily available in finely divided form or
- readily soluble in aqueous media

there will be advantages. Both of these forms allow the additive to be intimately mixed with the raw material, maximizing the contact surface area between the fluoride and the "fluoride trap".

Typical chemical cost and potential suppliers, of all the additives listed in Table 1, are listed in Table 4. There is a wide variation in both the price and availability of these additives. Since clay bricks are a relatively low priced product, expensive additives would normally be avoided.

4.3 Literature Study on the Use of Additives for Densification

The theory proposed in the literature concerning densification is that any gaseous fluoride can be trapped in the pore structure of the brick, given sufficient reduction in brick porosity. Empirical data presented by Scholze (25) and Routschka and Majdic (26) support this theory. In the former, a remarkable reduction in fluoride emission may result if the brick porosity is less than one volume percent. In the latter publication, the fluorine content of fired brick was measured as a function of pore volume. The fluoride content of the brick decreased in an exponential type function with increasing porosity. At a porosity of about 12%, the fluorine emissions begin to decrease until they reach a minimum at the lowest porosity obtained (about 3%).

The CANOLE literature search resulted in a total of 1,068 titles being printed, however the majority of these concerned the densification of high performance ceramics during hot pressing and/or sintering. A total of 40 titles were considered sufficiently relevant to obtain the abstracts.

Thirty of these 40 abstracts contained useful information with the majority dealing with specific deflocculants in specific clays.

Four reviews concerning clay deflocculation were obtained. Schueller and Herold(27) discuss the effects of deflocculants and pH on casting and strength properties while the process and mechanism of deflocculation is reviewed by Baudet(28), Malandrino(29) and Satava(30).

As previously stated, many papers discuss specific deflocculants(31-50). These deflocculants, along with the references, are given in Table 5.

Two of the papers(51, 52) describe studies concerned with the rheological properties of clay slurries where the effects of particle size distribution(51), pH(51), solids contents(52) and degree of deflocculation(52) were included.

Finally, three of the abstracts deal with ceramic densification through control of particle size distribution. Yan et al(53) state that a narrow grain size distribution can yield sintered densities of approximately 99.3% compared to approximately 90.6% with a nonuniform grain size distribution. Brick density was increased by Abbakumov et al (54) by using grain sizes of 0.5 -2 mm, and a brick density of 88% was achieved by Albert et al(55) by using particle diameters ranging from approximately 15-25 mm.

4.4 Experimental Program on Chemical Additives

In general, the program to evaluate the effect of chemical additives on fluoride suppression has met with mixed results; in some cases, fluoride evolution was suppressed, in others it was accelerated. In both cases, however, the percentage change was generally too small to warrant serious consideration of this technique as a means of controlling fluoride evolution. Only sample 107 showed benefits for all additions used and these were significant, minimum benefits being 33% suppression. The results are shown in Tables 6, 7 and 8. Table 6 shows the fluoride loss data obtained by the Institut Für Ziegelforschung in Essen, using actual brick specimens. Tables 7 and 8 show data from the experimental firings using additives as possible fluoride - evolution suppressants in Phase B of this study.

4.4.1 Chemical Additives to Suppress Fluoride Evolution

The addition of cerium oxide, the alkaline earth carbonates and calcium hydroxide provided no technical difficulties for the extrusion operation, and were routinely handled. The deflocculants gave some cause for concern and one run had to be aborted due to major power fluctuations on the extrusion machine caused by 'setting-up' in the barrel of the extruder. This effect is significant in that the 'setting-up' action coupled with the action of the extruder generated enough force to break the main auger screw flight.

The observed effects of ten additives on the suppression of fluoride evolution suggest that with the exception of sample #107 they are relatively ineffective. For this particular sample significant benefits were observed for additions of Cerium Oxide, Strontium Carbonate, and Barium Carbonate (which is routinely used for 'scum' control by all brick manufacturers).

Sample #105 also showed significant benefits with the addition of $MgCO_3$ and to a lesser degree with the addition of calcium carbonate. Smaller benefits (10-12% reduction in emissions) were obtained upon addition of $CaCO_3$ and $MgCO_3$ to sample #103. An opposite trend, i.e. an increase in emissions was observed with the additions of cerium strontium and barium to sample #104.

4.4.2 Chemical Additives for Brick Densification

The addition of sodium carbonate/sodium silicate combinations and lignosulphonates to increase brick densification during extrusion were conducted on samples #103 and #105 in the case of sodium carbonate/sodium silicate and on samples #104 and #107 in the case of the lignosulphonate.

The sodium carbonate/sodium silicate combination provided slight benefits of 12% for samples #103 and #105.

The lignosulphonate addition gave rise to contradictory results for the two samples evaluated. Sample #104 showed an increase in fluoride evolution of 29% while sample #107 showed a distinct benefit of a suppression of 33%.

The results obtained for the sodium carbonate/sodium silicate additions are, as one would anticipate, partial deflocculation which would improve packing density of the clay particles during extrusion and improved densification, which in turn should cause some limitation in fluoride evolution. This is in keeping with ideas previously noted in the literature. Sodium silicate/sodium carbonate additions would also provide a small fluxing action on the clay/shale particles which should also aid in densification.

4.4.3 Porosity of Fixed Products

The porosity of the fired samples was measured using a Micromeritics Mercury Intrusion Porosimeter. The method involves the measurement of pore size distribution via the volume penetration of mercury into a sample as a function of mercury pressure. Pressures up to 60,000 psi yield information on pores down to 0.3 um in diameter. Porosimetry data are given in Table 9. The porosity of the samples ranges from 6.2 - 22.9%. The lowest porosities were observed in Sample #103; each of the additives reduced the porosity. Furthermore Sample #103 had a lower porosity than Sample #105 even though both had similar moisture contents when extruded. Pore size distribution determined by mercury porosimetry, for each sample with and without additives is shown by the data contained in Appendix 3.

PHASE B

CONCLUSIONS AND RECOMMENDATIONS

5. CONCLUSIONS & RECOMMENDATIONS

The objective of this study was to produce recommended methods of reducing fluoride emissions from brick kilns. These methods would be applied at the first stage of brick manufacture, i.e. the selection of raw materials and the formation of the green brick. As outlined earlier, admixtures which would react with gaseous fluoride and brick densification are two possible routes to reduce fluoride emissions.

The literature search showed that published research in this area is limited with most papers and patents dealing with alkaline metal oxides, hydroxides and carbonates. Furthermore, the findings published by one researcher do not always concur with other published findings, and it is not possible to elucidate the causes of the discrepancies because of the potentially wide variation in starting materials and experimental methods.

There was, however, enough information to design a meaningful preliminary experimental program with Canadian clays and shale to study the effect of certain additives on their fluorine release during firing. This program involved the addition of:

- metal ions reported to reduce fluorine emissions
- metal ions anticipated to reduce fluorine emissions
- deflocculant to reduce brick porosity and consequently fluorine emissions

Data obtained is summarized as follows:

- The ability of a particular additive to reduce fluorine emissions was dependent on the particular clay/shale and firing curve used. All additives reduced emissions (to varying degrees) in samples #103, #105 and #107 whereas no additive reduced emissions in sample #104. Sample #104, however had extremely high fluoride retention in the blank sample and overall fluorine release ranged from 100-200 ppm during the firing whereas the overall release from the other samples ranged from 250 to 500 ppm.

- The addition of deflocculants decreased the porosity of the fired materials. In the case of samples #103 and #105, slight improvement in fluorine emissions was observed while a significant improvement was observed in sample #107. Sample #104 showed the opposite effect with a significant increase in fluorine emissions being observed.

From the data it is concluded that:

- The additives evaluated could be readily incorporated into the brick making process.

- The additives had a significant beneficial effect only in the case of sample #107.

- Despite high natural fluoride contents sample #104 shows minimal release of fluorine under all of the testing conditions. This is attributed to a natural combination of geological and chemical characteristics of the deposit, the manufacturing process and the kiln firing profile.

- With the exception of sample #104 the addition of deflocculants densified the brick structure with a minimal decrease in fluorine emissions.

- Denser products will minimize fluoride evolution. In general terms the natural properties of the raw material coupled with the manufacturing conditions will override or dominate over the effects of any additives.

TABLES

TABLE 1

PHYSICAL PROPERTIES OF INORGANIC FLUORINE CONTAINING COMPOUNDS

Atom	Fluorine Containing Compound	Melting Point(°C)	Decomposition Point(°C)	Comments
Li	LiF	842	1676	
	$Li_2SiF_6.2H_2O$	100	-	Dehydrates, then decomposes
Be	BeF_2	800	-	Sublimes at 800°C
Na	NaF	988	1695	
	Na_2SiF_6	-	-	Decomposes
Mg	MgF_2	1266	2239	
	$MgSiF_6$	-	-	
	$MgSiF_6.6H_2O$	-	-	Decomposes at 120°C
Al	AlF_3	1291	-	Sublimes at 1291°C
	$2AlFO.SiO_2$	-	-	Naturally-occurring as topaz
K	KF	846	1505	
	K_2SiF_6	-	-	
Ca	CaF_2	1360	2500	
	$CaSiF_6$	-	-	
	$CaSiF_6.2H_2O$	-	-	Decomposes in water
Ti	TiF_4	>400	284	M.P. under pressure
	TiF_3	1200	1400	
V	VF_5	-	111.2	
	VF_4	325	-	Decomposes
	VF_3	>800	-	Sublimes
Cr	CrF_2	1100	>1300	
	CrF_3	>1000	1100-1200	Sublimes
Mn	$MnSiF_6.6H_2O$	-	-	Decomposes
	MnF_2	856	-	
	MnF_3	-	-	Decomposes
Fe	FeF_2	>1000	-	
	FeF_3 or	>1000	-	
	Fe_2F_6	>1000	-	
	$FeSiF_6.6H_2O$	-	-	

Table 1 (continued)

Atom	Fluorine Containing Compound	Melting Point(°C)	Decomposition Point(°C)	Comments
Co	CoF_2	1200	1400	
	CoF_3	-	-	Decomposes to $Co(OH)_3$ in H_2O
	$CoF_2.4H_2O$	-	-	Decomposes at 200°C
	$CoSiF_6.6H_2O$	-	-	
Ni	NiF_2	1000	-	Sublimes in HF
	$NiSiF_6.6H_2O$	-	-	Decomposes
Cu	CuF	908	1100	Sublimes at 1100°C
	CuF_2	950	-	Decomposes
	Cu_2SiF_6	-	-	
	$CuSiF_6.4H_2O$	-	-	
	$CuSiF_6.6H_2O$	-	-	
Zn	ZnF_2	872	1500	
	$ZnF_2.4H_2O$	100	-	Dehydrates
	$ZnSiF_6.6H_2O$	100	-	Decomposes
Ga	GaF_3	800 (sublimes)	~1000	
	$GaF_3.3H_2O$	-	-	$-H_2O$ at 140°C in vacuum
Ge	GeF_2	>350	Sublimes	Decomposes
	GeF_4	-37		
	$GeF_4.3H_2O$	Decomposes		
As	AsF_5	-80	-53	
	AsF_3	-8.5	-63	
Se	SeF_6	-39	-34.5	
	SeF_4	-13.8	>100	
Rb	RbF	775	1410	
	Rb_2SiF_6	-	-	
	$RbSFO_3$	304	-	
Sr	SrF_2	1450+	2489	
	$SrSiF_6.2H_2O$	Decomposes		
Y	YF_3	1387		
Zr	ZrF_4	~600	-	Sublimes
Nb	NbF_5	72-73	236	

Table 1 (continued)

Atom	Fluorine Containing Compound	Melting Point(°C)	Decomposition Point(°C)	Comments
Mo	MoF_6	17.5	35	
Ru	RuF_5	101	250	
Rh	RhF_3	>600	-	Sublimes
Pd	PdF_2	-	-	Volatile, decomposes in red heat
	PdF_3	-	-	Decomposes
Ag	AgF	435	~1159	
	AgF_2	690	700	Decomposes
	Ag_2F	90	-	Decomposes
	$Ag_2SiF_6.4H_2O$	>100	-	Decomposes
Cd	CdF_2	1100	1758	
	$CdSiF_6.6H_2O$	-	-	
In	InF_3	1170	>1200	
Sn	SnF_2	-	-	
	SnF_4	705	-	Sublimes
Sb	SbF_5	7	149.5	
	SbG_3	292	319	Sublimes
Te	TeF_6	-36	35.5	
	TeF_4	-	>97	Sublimes
Cs	CsF	682	1251	
	Cs_2SiF_6	-	-	
Ba	BaF_2	1280	2137	
	$BaSiF_6$	300	-	Decomposes at 300°C
Ce	CeF_3	1460	2300	
	$CeF_4.H_2O$	~650	-	Decomposes
Nd	NdF_3	1410	2300	
Sm	SmF_2	1306	>2400	
	SmF_3	1306	2323	
Eu	EuF_2	1380	>2400	
	EuF_3	1390	2280	

Table 1 (continued)

Atom	Fluorine Containing Compound	Melting Point(°C)	Decomposition Point(°C)	Comments
Gd	GdF_3	-	-	
Tb	TbF_3	1172	2280	
Dy	DyF_3	1360	>2200	
Ho	HoF_3	1143	>2200	
Er	ErF_3	1350	2200	
Tm	TmF_3	1158	2200	
Yb	YbF_2	1052	2380	
	YbF_3	1157	2200	
Lu	LuF_3	1182	2200	
Hf	HfF_4	-	-	
Ta	TaF_3	96.8	229.5	
W	WF_6	2.5	17.5	
Re	ReF_4	124.5	500	
	ReF_6	18.8	47.6	
Os	OsF_6	32.1	45.9	
	OsF_4	-	-	
Ir	IrF_6	44.4	53	
Pt	PtF_6	57.6	-	
	PtF_4	-	-	Decomposes in red heat
Hg	Hg_2F_2	570	-	
	HgF_2	645	650	
	$Hg_2SiF_6.2H_2O$	-	-	
	$HgSiF_6.6H_2O$	-	-	Easily decomposes
Tl	TlF	327	655	
	TlF_3	550	-	Decomposes at 550°C
	$Tl_2SiF_6.2H_2O$	-	-	
Pb	PbF_2	855	1290	
	$PbSiF_6.2H_2O$	-	-	Decomposes
	$PbSiF_6.4H_2O$	-	-	Decomposes at <100°C

Table 1 (continued)

Atom	Fluorine Containing Compound	Melting Point(°C)	Decomposition Point(°C)	Comments
Bi	BiF_3	727	-	
Ac	AcF_3	-	-	
Th	ThF_4	900	-	
	$ThF_4.4H_2O$	$-H_2O$, 100	$-2H_2O$ 140-200	
Pa	PaF_4	-	-	
U	UF_6	64.5	56.2	
	UF_4	960	-	
	UF_3	-	-	Decomposes above 1000

TABLE 2

DETAILS OF MIXES

Sample	Additive	Weight Clay-Shale (kg)	Weight Additive (g)	Volume Water (ml)	Extruded Moisture Content (%)
#104	Blank	6.0	-	923	13.9
	CeO_2	5.95	54	1,000	14.1
	$BaCO_3$	5.90	96	1,000	14.7
	$SrCO_3$	5.93	72	1,000	14.6
	$Ca(OH)_2$	5.97	35	~1,000	15.6
	Lignosol SF*	6.0	60	1,000	14.5
#107	Blank	6.0	-	790	11.2
	CeO_2	5.93	66	750	13.1
	$BaCO_3$	5.89	108	790	BA1 12.4
					BA2 12.1
	$SrCO_3$	5.92	84	~790	12.0
	$Ca(OH)_2$	6.0	40.8	~790	13.5
	Lignosol SF*	6.0	19.8	~790	12.7
#103	Blank	6.0	-	790	17.5
	$CaCO_3$	5.96	36	790	16.4
	$MgCO_3$	5.97	30	~790	16.0
	$SrCO_3$	5.95	48	~790	17.3
	$CA(OH)_2$	5.98	25	~790	15.9
	Na_2SiO_3/Na_2CO_3	6.0	12	~790	17.6
#105	Blank	6.0	-	-	16.7
	$CaCO_3$	7.37	42	-	16.7
	$MgCO_3$	7.38	36	-	17.5
	$Ca(OH)_2$	7.38	31.8	-	19.9
	$SrCO_3$	7.34	66	-	18.1
	Na_2SiO_3/Na_2CO_3	7.42	6	-	16.9

* Sugar-free calcium lignosulfonate

TABLE 3

PHYSICAL PROPERTIES OF SELECTED METAL SALTS

Atom	Fluorine Containing Compound	Melting Point	Decomposition Point	Comments
Mg	MgO	2800	3600	Soluble in acid, NH_4 salts
Al	Al_2O_3	2045	2980	Insoluble
	Corundum	2015	2980	Insoluble (also is Al_2O_3)
Ca	$CaCO_3$	-	898	Decomposes to CaO
	CaO	2580	2850	
Ti	TiO_2	1830	2500-3000	
Sr	$SrCO_3$	1497	-	$-CO_2$ at 1340°C
Y	Y_2O_3	2410	-	-
	Y_3FesO_{12}			
Ba	$BaCO_3$	1740	d1450	Melting point at 90 atm, decomposes
	$Ba(OH)_2.8H_2O$	1923	2000	$-8H_2O$ at 780°C
Ce	CeO_2	2600	-	
	$Ce(OH)_4$	-	-	$-2H_2O$
Nd	Nd_2O_3	1980	-	
	$Nd_2O_3.TiO_2$	-	-	
Sm	Sm_2O_3	-	-	
Eu	Eu_2O_3			
Dy	Dy_2O_3	2340		
Er	Er_2O_3	infusible		

TABLE 4

AVAILABILITY AND COST OF POTENTIAL ADDITIVES

Additive	Cost ($/kg)	Supplier
Magnesium Oxide	0.97	Canada Colours
Magnesium Carbonate	0.227	Can Wafers-Rogers
Magnesium Hydroxide	5.51	Mallenkrodt Chemical
Aluminum Oxide	3.86	Kingsley and Keith
Calcium Oxide	0.114	Beachville Lime Ltd.
Calcium Hydroxide	0.10	Beachville Lime Ltd.
Calcium Carbonate	0.06	Beachville Lime Ltd.
Titanium Dioxide	2.10	Kingsley and Keith
Strontium Carbonate	-	No Canadian bulk supplier
Yttrium Oxide	-	No Canadian bulk supplier
Barium Carbonate	0.55	Canada Colours
Barium Hydroxide	1.60	Kingsley and Keith
Cerium IV Oxide	17.00	W. R. Grace

TABLE 5

CHEMICALS USED TO DEFLOCCULATE CLAYS

Deflocculant	References
Na_2SiO_3	31, 32, 34-38, 41, 42, 44, 49
$Na_2P_2O_7$	31, 39, 41-43
Na_2CO_3	32, 35, 38, 39, 44
$NaHCO_3$	33
$Na(OH)$	32-34
Sodium tannate	36, 37
Sodium oxalate	32
Sodium humate	33
Calgon	34
Polyacrylates	35-37, 41, 42, 44
Polyacrilimides	39, 40, 45
Polyacrilic acid	46
"Organosilicon"	40
Lignosulfonates	40
"Tanning agents"	40
$(NH_4)_2C_2O_4$	40
Triethanolamine	40
Acetyl carboxylate	47
$Al_2(SO_4)_3/NaOH$	48
Anionic dyes	50

TABLE 6: TEST DATA FROM INSTITUTE FÜR ZIEGELFORSCHUNG

SAMPLE	EXPECTED FLUORIDE (mg/kg)			LOSS
#	RAW	FIRED	LOSS	(%)
103	690	70	620	90
104	930	790	140	15
105	890	610	280	31
107	1150	580	570	50

TABLE 7: EFFECTS OF ADDITIVES ON FLUORIDE SUPPRESSION

		FLUORIDE REMAINING AFTER FIRING (mg/kg)							
SAMPLE #	BLANK	CERIUM (Ce)	STRONTIUM (Sr)	BARIUM (Ba)	CALCIUM (Ca coarse)	CALCIUM (Ca fine)	MAGNESIUM (Mg)	SODIUM (Na)	LIGNOSOL (L)
103	323		463		356	513	363	363	
104	1125	1013	938	919		825			800
105	525		625		575	475	650	588	
107	448	738	628	595		650			595

TABLE 8: NET CHANGE IN FLUORIDE LOSS WITH ADDITIVES

SAMPLE #	BLANK	CERIUM (Ce)	STRONTIUM (Sr)	BARIUM (Ba)	CALCIUM (Ca coarse)	CALCIUM (Ca fine)	MAGNESIUM (Mg)	SODIUM (Na)	LIGNOSOL (L)
		RELATIVE FLUORIDE LOSS COMPARED TO BLANK (%)							
103	100		-43	0	-10	-59	-12	-12	
104	100	10	17	10		27			29
105	100		-19		-10	10	-24	-12	
107	100	-65	-40	-33		-45			-33

NOTE: (-) Reduction in Fluoride Loss
(+) Increase in Fluoride Loss

TABLE 9

POROSIMETRY DATA

Sample No.		Porosity (%)
105	Blank	22.9
	$MgCO_3$	20.9
	Na_2CO_3/Na_2SiO_3	21.7
	$CaCO_3$	21.0
	$Ca(OH)_2$	30.6
103	Blank	12.6
	$MgCO_3$	8.6
	Na_2CO_3/Na_2SiO_3	6.2
	$CaCO_3$	9.9
	$SrCO_3$	10.3
	$Ca(OH)_2$	13.9
107	Blank	17.1
	$SrCO_3$	11.9
	Lignosol	15.0
	CeO_2	17.7
	Ba_2CO_3	16.5
	$Ca(OH)_2$	26.2
104	Blank	21.6
	Lignosol	13.6
	$SrCO_3$	25.9
	$BaCO_3$	28.1
	CeO_2	21.3
	$CaOH_2$	30.0

FIGURES

Figure 1

Deflocculation Curves of Starting Materials

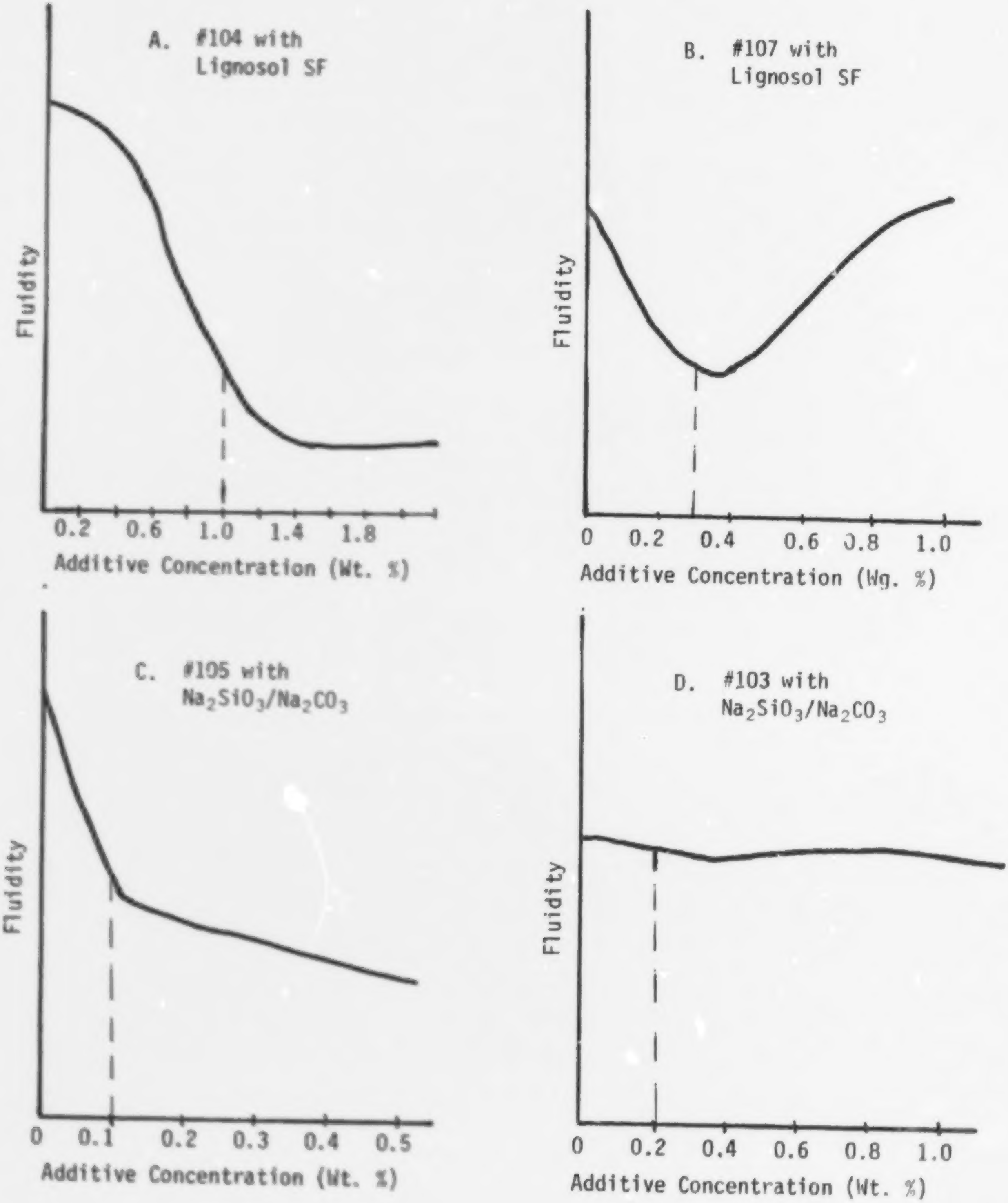
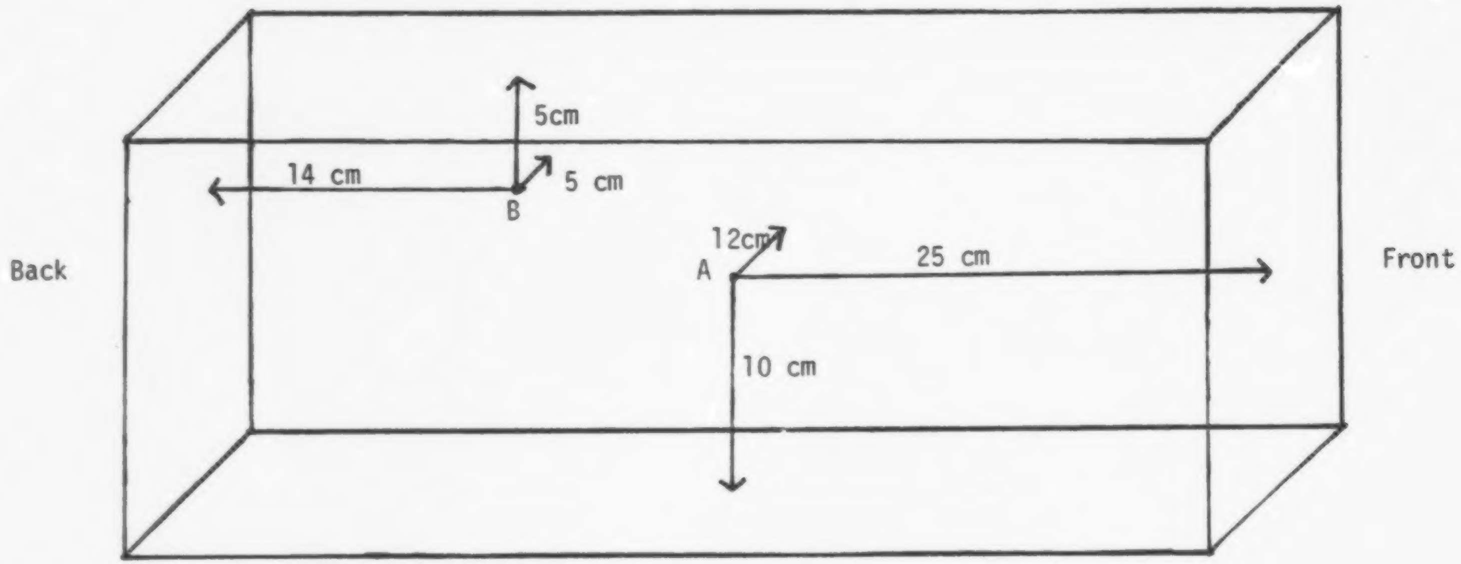


Figure 2

Position of Thermocouples in Muffle Furnace


5cm
14 cm
5 cm
B
12cm
A
25 cm
Back
Front
10 cm

APPENDICES

- References
- Test Kiln Firing Curves
- Pore Size Distribution Data

APPENDIX 1

REFERENCES

5.1 References

1. Troll, G. and Farzaneh, A., "Fluorine Loss in Production of Bricks and Comparison with the Loss in Fluorine-bearing Minerals", Interceram, Vol. 27, No. 3, p. 300, 1978.

2. Luxon, S.G., "Fluoride Emission During Firing of Pottery in Continuous Kilns", Fluoride Vol. 3, p. 61, 1970.

3. Tunker, G. and Schmidt, H., "Solution to a Fluorine Emission Problem in Stoneware Production", Ziegelindustrie Int. 3, p. 173, 1982.

4. Kother, W. and Pauls, N., "Determination of a Production Firing Curve for Optimum Fluorine Bonding in Brick Firing", Ziegelindustrie Int. 3 p. 167, 1982.

5. Routschka, G., Buttgerist, C. and Berger, U., Sprechsaal 103 901, 1970.

6. Routschka, C. and Majdic, A., "Studies on the Behavious of Fluoride in the Firing of Refractory Clays", Ziegelindustrie Int. No. 4, p.227, 1979.

7. Routschka, C. and Majdic, A., "Fluoride Emission in the Kiln Firing of Refractory Clays to Chamotte", Ziegelindustrie Int. No. 1, p. 6, 1978.

8. Smidt, H., "Fluoride - central problem for the brick and tile industry in the sector of clearn air", Ziegelindustrie Int. No. 4, p. 165, 1977.

9. R. Graetz, Ziegelindustrie, 1974, (4), 164-8.

10. H. Kolkmeier, Handbuck fur die Zieglindustrie: ver fahren und Betriebsprakis in der Grabkeramik, Bauverlag Wiesbaden, Berlin 1982, 522-531.

11. P. Mazzali, G. Fogliani, L. Orlandi and G. Busani, Ceramica (Florence), 1980, 33(2), 1-6.

12. W. Handl, E. Luberknacht and B. Morczynski, German Patent 3,016,431, Nov. 5, 1981.

13. K. Bergmann and F. Troyer, Ziegelindustrie, 1972, (5) 234-40.

14. H. Iseke and E. Lazit, German Patent 2,723,712, Dec. 7, 1978.

15. A. Haessler, German Patent 2,754,854, June 13, 1979.

16. G. Tuenker and H. Schmidt, Keram.Z, 1983, 35(7), 347-50.

17. W. Koelling, W.W. Wolfram, E. Heinrich, German Patent 2,139,334, July 13, 1972.

18. W. Koelling, W. Wolfram and E. Heinrich, British Patent 1,351,690, May 1, 1974.

19. V. Goncharenko, V. Kurkin, V. Volobuer and A. Denisenko, Prom. Sanit. Orchistka Gazov, 1978, (5), 2-3.

20. H. Kolkmeier, Z. I. Int., 1979 (11), 670-4.

21. E. Schmidt, Gas Waerme Int., 1975, 24(4), 150-6.

22. B. Byer, C. Wong and R. Yang, Environ. Sci. Technol., 1983, 17, 84-88.

23. C. Routschka and A. Majdic, Z.I. Int., 1978, (2) 75-86.

24. A. Frazier, J. Lehr and E. Dillard, Environ. Sci. Technol., 1977, 10, 1007-1014.

25. H. Schmidt, H. Scholze, G. Tunker, Science of Ceramics, Vol, 11, 333-339, 1981.

26. G. Routschka and A. Majdic, Z.I. Int., Jan. 1978.

27. K. Schueller and U. Herold, Keram Z., 1983, 35(12), 634-7).

28. G. Baudet, Ind. Ceram., 1981, 753, 627-34.

29. Q. Malandrino, Ceram. Inf., 1976, (11), 124, 693-700.

30. V. Satava, Ind. Ceram. 1977, 707, 433-7.

31. M. Gal'perina and Z. Safronova, Steklo Keram., 1973, (12), 21-2.

32. W. Ryan, Trans. Brit. Ceram. Soc., 1970, 69(1), 33-6.

33. B. Jiri, S. Dalibor, D. Stanislav and R. Vaclav, French Patent 1,482,794, May 26, 1967.

34. S. Gunasekera and W. Ryan, Trans. J. Br. Ceram. Soc., 1974, 73(5), 147-51.

35. E. Alston, Trans. J. Br. Ceram. Soc., 1975, 74(8), 279-83.

36. G. Bigelow and S. Prokopovich, Proc.-Aust. Ceram. Conf., 1976, 7, 48/1.

37. G. Bigelow and S. Prokopovich, J. Aust. Ceram. Soc., 1977, 13(2), 31-4.

38. W. German, Ceramica (Sao Paulo), 1978, 24(97), 36-8.

39. J. Chapman, D. Anderson, Brazil Patent 79 01,249, March 18, 1980.

40. I. Orlova, N. Dryda and E. Lisovaya, Ogneupary, 1980, (6), 32-6.

41. B. Soldavini, Ceram. Inf., 1976, 11(114), 71-4.

42. A. Marques, Ceramica (Sao Paulo), 1980, 26(132), 393-461.

43. M. Gilde and Z. Repasi, Kolloidkern Konf. Eloadasai, 3RD, 1981, 274-7.

44. P. Jadlicka, Sklar Keram, 1983, 33(3), 65-9.

45. Y. Atia, Int. J. Miner Process, 1983, 10(3), 173-81.

46. Taiko Refractories Co. Ltd., Japanese Patent 58,101,006, June 16, 1983.

47. M. Crutchfield, U.S. Patent 4,326,189, Apr. 27, 1982.

48. J. Bidwell, R. Adams and W.Jepson, U.S. Patent 4,095,235, Aug. 30, 1977.

49. P. Vycudilik, Sklar Keam., 1974, 24(7), 201-8.

50. S. Srivastava, S. Kumar, P. Razdan, Indian J. Chem. Sect. A. 1978, 16A(8), 688-91.

51. E. Monteiro, F. Angelar, Ceramica (Sao Paulo), 1980, 26(125), 93-103.

52. R. Lapasin and E. Lucchini, Ceramurzie, 1981, 11(2), 57-61.

53. M. Yan, R. Cannon and H. Bowen, Mater. Sci. Eng., 1983, 60(3), 275-81.

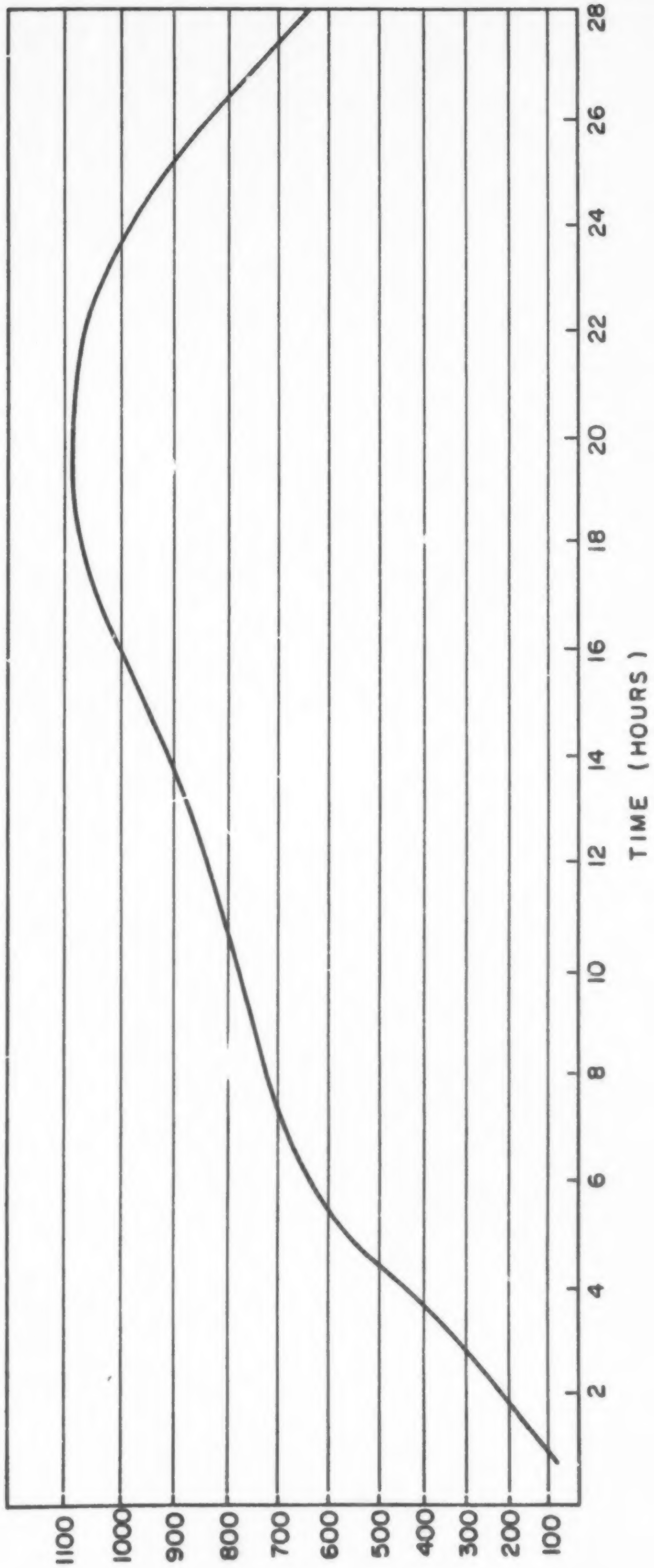
54. V. Abbakumov, M. Glazman and E. Degtyareva, Ot. Iz. Prom. Obraztsy, 1978, 55(3), 71.

55. R. Albert, and J. Robinson, German Patent 1,938,803, March 12, 1970.

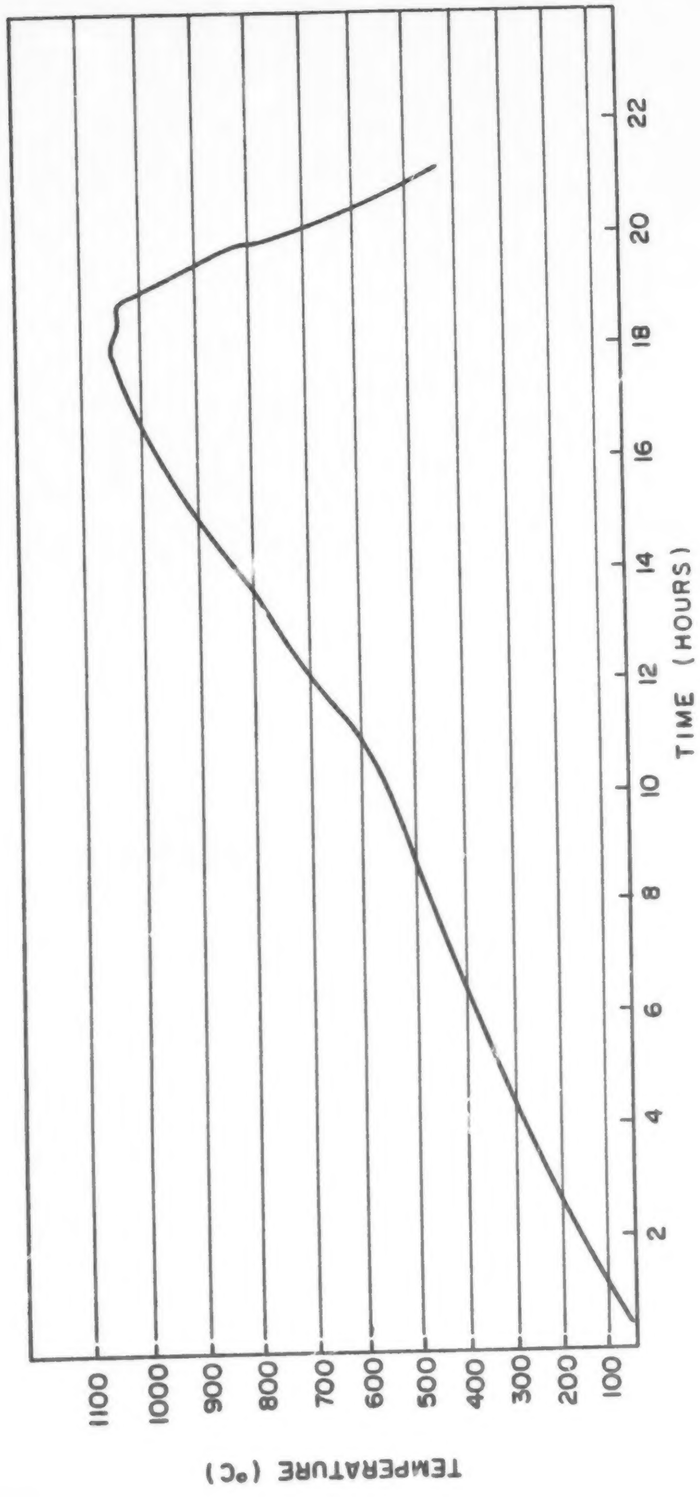
APPENDIX 2

TEST KILN FIRING CURVES

FURNACE TEMPERATURE PROFILE
SAMPLE 103

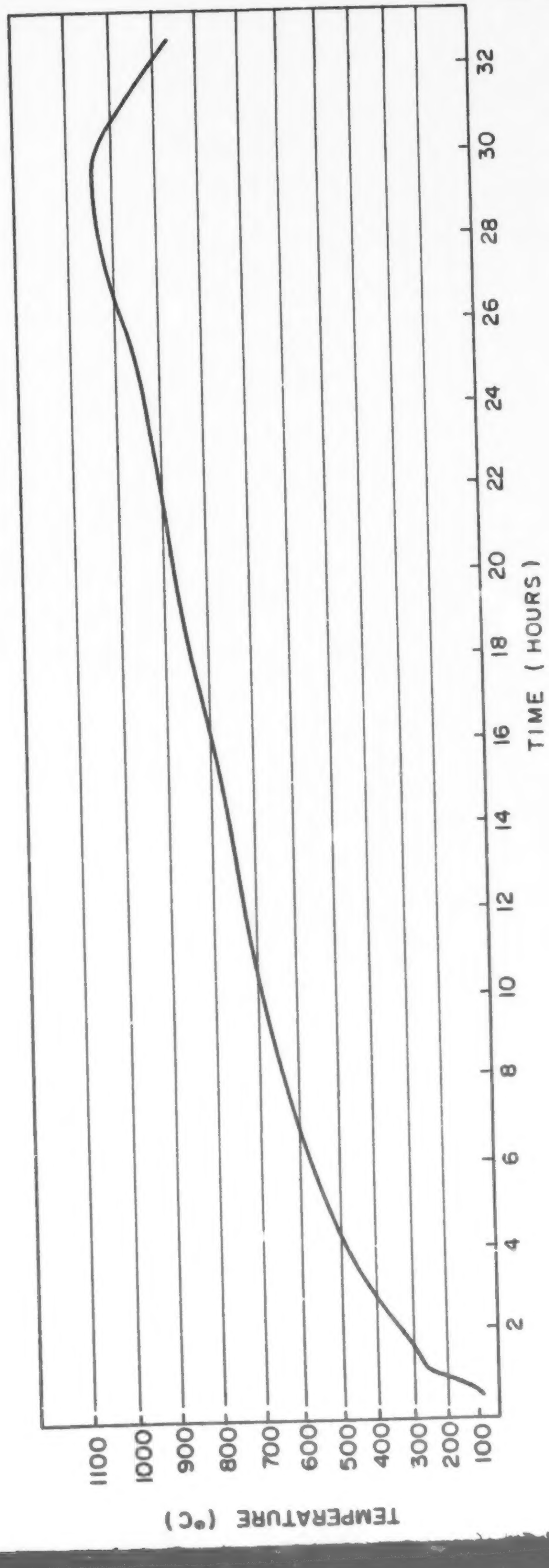


FURNACE TEMPERATURE PROFILE
SAMPLE 104

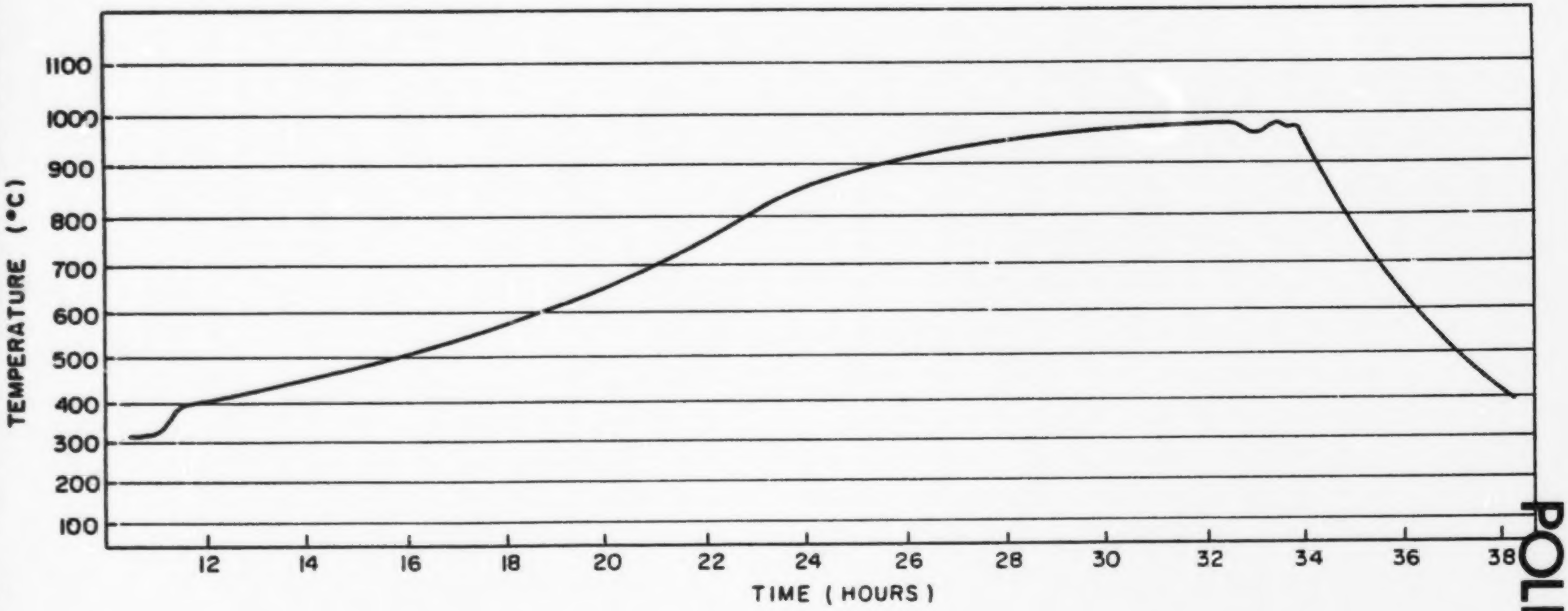


POLLUTECH

FURNACE TEMPERATURE PROFILE
SAMPLE 105



FURNACE TEMPERATURE PROFILE
SAMPLE 107



APPENDIX 3

PORE SIZE DISTRIBUTION DATA

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                  PAGE 6

ONTARIO RESEARCH FPL                                        LP 16:39:37 4/15/85
#103 CLAY CA                                                HP 17:2:18 4/15/85
NTR NUMBER   +21

                   INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.430531E-002

         0%           20%           40%           60%           80%          100%
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-**
    +144-*******
    +113-***********
   +88.1-***************
   +69.0-*********
   +54.0-*******
   +42.3-*******
   +33.1-****
   +25.9-***
   +20.3-**
   +15.9-***
   +12.4-***
   +9.72-****
   +7.61-**
   +5.96-*
   +4.66-**
   +3.65-****
   +2.86-*****
   +2.24-********
   +1.75-*********
   +1.37-*************
   +1.07-*********************
  +0.839-***********************************************
  +0.657-**********************************************************************
  +0.514-********************************
  +0.402-************************
  +0.315-************************************
  +0.247-**************************
  +0.193-********************************
  +0.151-********************************
  +0.118-******************
 +0.0926-**********
 +0.0725-*************
 +0.0567-********
 +0.0444-********
 +0.0347-*****
 +0.0272-*****
 +0.0213-*****
 +0.0167-*****
 +0.0130-*****
 +0.0102-*****
 0.00799-****
+0.00626-****
+0.00490-****
 0.00383-*****
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                    PAGE 6

ONTARIO RESEARCH FPL                                             LP 16:39:37 4/15/85
#[illegible]3. CLAY  MG                                                    HP 8:47:20 4/16/85
PNTR NUMBER    +15

                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                 100% = +0.374001E-002

            0%          20%           40%           60%           80%           100%
            I............I.............I.............I.............I.............I
      +300-*
      +235-*
      +184-*
      +144-*****
      +113-*******
     +88.1-*********
     +69.0-******
     +54.0-****
     +42.3-**
     +33.1-*
     +25.8-*
     +20.3-**
     +15.9-*
     +12.4-**
     +9.72-**
     +7.61-*
     +5.96-*
     +4.66-*
     +3.65-*
     +2.86-*
     +2.24-*
     +1.75-**
     +1.37-****
     +1.07-****
    +0.839-*********
    +0.657-*******************
    +C.514-*******************
    +0.402-******************************
    +0.315-*****************************************************
    +0.247-**********************************************************
    +0.153-**********************************************************************
    +0.151-*******************************************************
    +0.116-**************************
   +0.0926-*************
   +0.0725-*****************
   +0.0567-*********
   +0.0444-*********
   +0.0347-*
   +0.0272-*****
   +0.0213-******
   +0.0167-*****
   +0.0130-*****
   +0.0102-******
   0.00799-*****
   0.00626-*******
   0.00490-*************
  +0.00383-*************
   0.00300-*
```

```
                     MICROMERITICS AUTO-PORE 9200 V2.02                          PAGE 6

NTARIO RESEARCH FPL                                                          LP 16:39:37 4/15/85
03 CLAY NA                                                                   HP 8:47:20 4/16/85
PNTR NUMBER     +6


                     INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                    100% = +0.334520E-002

         0%          20%           40%           60%           80%          100
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-******
    +113-**********
   +86.1-*************
   +69.0-********
   +54.0-******
   +42.3-****
   +33.1-***
   +25.9-**
   +20.3-*
   +15.9-**
   +12.4-**
   +9.72-**
   +7.61-*
   +5.56-*
   +4.66-*
   +3.65-***
   +2.86-***
   +2.24-****
   +1.75-****
   +1.37-******
   +1.07-*****
  +0.839-*********
  +0.657-***********************
  +0.514-***********************
  +0.402-*****************************************
  +0.315-**********************************************************************
  +0.247-**************************************************************
  +0.193-**********************************************************
  +0.151-**********************
  +0.118-*
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
+0.00799-*
 0.00626-*
 0.00490-*
+0.00383-*
 0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                 PAGE 6

NTARIO RESEARCH FPL                                          LP 16:39:37 4/15/85
#103 CLAY BLANK                                              HP 17:2:18 4/15/85
NTR NUMBER    +37

                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.810233E-002

          0%           20%           40%           60%           80%          100%
          I............I.............I.............I.............I.............I
   +300-*
   +235-*
   +184-*
   +144-****
   +113-*******
  +86.1-*********
  +69.0-****
  +54.0-***
  +42.3-**
  +33.1-**
  +25.9-*
  +20.3-*
  +15.9-*
  +12.4-**
  +9.72-*
  +7.61-*
  +5.96-*
  +4.66-*
  +3.65-**
  +2.86-*****
  +2.24-*************
  +1.75-********************************************************
  +1.37-**********************************************************************
  +1.07-***************************************
 +0.839-*****************************
 +0.657-******************
 +0.514-******
 +0.402-*****
 +0.315-********
 +0.247-******
 +0.193-**********
 +0.151-***********
 +0.118-******
+0.0926-****
+0.0725-******
+0.0567-****
+0.0444-****
+0.0347-***
+0.0272-***
+0.0213-***
+0.0167-**
+0.0130-***
+0.0102-***
0.00799-***
+0.00626-***
+0.00490-*****
0.00383-******
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                   PAGE 6

ONTARIO RESEARCH FPL                                          LP 11:27:52 4/18/85
03 CLAY CA(OH)2                                               HP 12:1:22 4/18/85
NTR NUMBER    +21


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.413457E-002

         0%          20%           40%           60%           80%           100%
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*********
    +113-***************
   +88.1-********************
   +69.0-**************
   +54.0-**********
   +42.3-*******
   +33.1-******
   +25.9-******
   +20.3-******
   +15.9-*******
   +12.4-******
   +9.72-********
   +7.61-***
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-****
   +2.24-***************
   +1.75-***************************
   +1.37-**********************************************************
   +1.07-**********************************************************************
  +0.839-**************************************************************
  +0.657-**************************************************
  +0.514-*****************
  +0.402-***************
  +0.315-**********************
  +0.247-*******************
  +0.193-****************************
  +0.151-**************************
  +0.118-***************
 +0.0926-************
 +0.0725-****************
 +0.0567-*********
 +0.0444-*************
 +0.0347-********
 +0.0272-**********
 +0.0213-***********
 +0.0167-***********
 +0.0130-**************
 +0.0102-*******************
+0.00799-*******************
+0.00626-********************
+0.00490-******************************
+0.00383-********************************
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                  PAGE 6

ONTARIO RESEARCH FPL                                          LP 14:29:19 4/17/85
#103  CLAY SRC03                                              HP 8:49:6 4/18/85
NTR NUMBER    +23


                       INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.313512E-002

        0%            20%           40%           60%           80%           100%
        I.............I.............I.............I.............I.............I
    +300-*
    +235-**
    +184-***
    +144-******
    +113-*********
   +88.1-***********
   +69.0-***********
   +54.0-*********
   +42.3-******
   +33.1-****
   +25.9-***
   +20.3-***
   +15.9-*******
   +12.4-****
   +9.72-**
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*****
   +2.86-*****
   +2.24-***********
   +1.75-*********
   +1.37-***********
   +1.07-****************
  +0.839-************************
  +0.657-***********************************************
  +0.514-***********************************
  +0.402-******************************************
  +0.315-**********************************************************************
  +0.247-*********************************************************
  +0.193-*********************************************************
  +0.151-*******************************************************
  +0.118-******************************
 +0.0926-*************
 +0.0725-*********************
 +0.0567-***************
 +0.0444-***************
 +0.0347-*******
 +0.0272-**********
 +0.0213-*******
 +0.0167-******
 +0.0130-***********
 +0.0102-**************
+0.00799-***********
+0.00626-***********
+0.00490-************************
+0.00383-*********************
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                         PAGE 6

ONTARIO RESEARCH FPL                                                  LP 14:29:19 4/17/85
 05   CLAY SRC03                                                      HP 8:49:6 4/18/85
NTR NUMBER    +40


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.236090E-001

           0%           20%           40%           60%           80%           100%
           I............I.............I.............I.............I.............I
      +300-*
      +235-*
      +184-*
      +144-*
      +113-*
     +88.1-*
     +69.0-*
     +54.0-*
     +42.3-*
     +33.1-*
     +25.9-*
     +20.3-*
     +15.9-*
     +12.4-*
     +9.72-*
     +7.61-*
     +5.96-*
     +4.66-*
     +3.65-*
     +2.86-*
     +2.24-*
     +1.75-*
     +1.37-**
     +1.07-****
    +0.839-*************************************************************
    +0.657-**********************************************************************
    +0.514-***************
    +0.402-*********
    +0.315-********
    +0.247-*****
    +0.193-*****
    +0.151-****
    +0.118-**
   +0.0926-*
   +0.0725-*
   +0.0567-*
   +0.0444-*
   +0.0347-*
   +0.0272-*
   +0.0213-*
   +0.0167-*
   +0.0130-*
   +0.0102-*
  +0.00799-*
  +0.00626-*
  +0.00490-*
  +0.00383-*
  +0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                          PAGE 6

ONTARIO RESEARCH FPL                                                 LP 11:27:52 4/18/85
05    CLAY CA(OH)2                                                   HP 12:1:22 4/18/85
NTR NUMBER    +37

                         INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                        100% = +0.292270E-001

         0%           20%           40%           60%           80%           100%
         I............I.............I.............I.............I.............I
   +300-*
   +235-*
   +184-*
   +144-*
   +113-**
  +88.1-***
  +69.0-*
  +54.0-*
  +42.3-*
  +33.1-*
  +25.9-**
  +20.3-*
  +15.9-**
  +12.4-*
  +9.72-*
  +7.61-*
  +5.96-*
  +4.66-*
  +3.65-*
  +2.86-*
  +2.24-*
  +1.75-*
  +1.37-**
  +1.07-****
 +0.839-********************************************************************
 +0.657-**********************************************************************
 +0.514-***********
 +0.402-*******
 +0.315-******
 +0.247-****
 +0.193-****
 +0.151-****
 +0.118-**
+0.0926-*
+0.0725-**
+0.0567-*
+0.0444-**
+0.0347-*
+0.0272-**
+0.0213-**
+0.0167-**
+0.0130-***
+0.0102-***
+0.00799-***
+0.00626-****
 0.00490-*******
+0.00383-********
+0.00300-*
```

```
                 MICROMERITICS AUTO-PORE 8200 V2.02                  PAGE 6

NTARIO RESEARCH FPL                                   LP 0:52:1 4/4/38
105   CLAY   Ca                                        HP 1:16:30 4/4/38
PNTR NUMBER    +40

                 INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                100% = +0.281405E-001

         0%           20%           40%           60%           80%           100
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +86.1-*
   +65.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-*
  +0.839-************************
  +0.657-**********************************************************************
  +0.514-********************
  +0.402-**********
  +0.315-*********
  +0.247-*****
  +0.193-*****
  +0.151-***
  +0.118-**
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
 0.00799-*
 0.00626-*
+0.00490-*
+0.00383-*
 0.00300-*
```

```
                     MICROMERITICS AUTO-PORE 9200 V2.02                   PAGE 6

ONTARIO RESEARCH FPL                                                LP 0:52:1 4/4/38
#105  CLAY    Na                                                    HP 1:16:30 4/4/38
NTR NUMBER   +23

                     INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.281744E-001

         0%           20%           40%           60%           80%           100%
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-**
  +0.839-***********************
  +0.657-**********************************************************************
  +0.514-*******************
  +0.402-**********
  +0.315-********
  +0.247-*****
  +0.193-****
  +0.151-****
  +0.116-**
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
+0.00799-*
+0.00626-*
 0.00490-***
+0.00383-**
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                      PAGE 6

ONTARIO RESEARCH FPL                                              LP 13:27:14 4/15/85
105    CLAY    MG                                                 HP 13:59:33 4/15/85
PNTR NUMBER    +40

                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.192202E-001

          0%          20%          40%          60%          80%          100%
          I............I............I............I............I............I
     +300-*
     +235-*
     +184-*
     +144-**
     +113-***
    +88.1-****
    +69.0-**
    +54.0-**
    +42.3-**
    +33.1-*
    +25.9-*
    +20.3-*
    +15.9-*
    +12.4-*
    +9.72-*
    +7.61-*
    +5.96-*
    +4.66-*
    +3.65-*
    +2.86-*
    +2.24-*
    +1.75-**
    +1.37-**
    +1.07-*******
   +0.839-*********************************************************************
   +0.657-**********************************************************************
   +0.514-****************
   +0.402-*********
   +0.315-********
   +0.247-******
   +0.193-******
   +0.151-*****
   +0.118-**
  +0.0926-**
  +0.0725-**
  +0.0567-*
  +0.0444-**
  +0.0347-*
  +0.0272-*
  +0.0213-*
  +0.0167-*
  +0.0130-*
  +0.0102-*
 +0.00799-*
  0.00626-*
  0.00490-**
 +0.00383-*
 +0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                   PAGE 6

ONTARIO RESEARCH FPL                                         LP 13:27:14 4/15/85
#05   CLAY BLANK                                             HP 13:59:33 4/15/85
PNTR NUMBER    +23


                        INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                      100% = +0.391337E-001

         0%           20%           40%           60%           80%           100%
         I............I.............I............I.............I............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-*
  +0.839-***********
  +0.657-********************************************************************
  +0.514-**************
  +0.402-*******
  +0.315-******
  +0.247-****
  +0.193-****
  +0.151-***
  +0.118-*
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
+0.00799-*
+0.00626-*
+0.00490-*
+0.00383-*
+0.00300-*
```

```
                  MICROMERITICS AUTO-PORE 8200 V2.02                  PAGE 6

 NTARIO RESEARCH FPL                                      LP 16:58:22 4/18/85
 104   SHALE CLAY BLANK                                   HP 17:20:3 4/18/85
PNTR NUMBER   +21

                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.183173E-001

         0%          20%           40%           60%           80%          100
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*****
    +113-********
   +88.1-**********
   +69.0-*********
   +54.0-*******
   +42.3-*****
   +33.1-***
   +25.9-****
   +20.3-***
   +15.9-***
   +12.4-**
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-**
   +1.75-***
   +1.37-****
   +1.07-******
  +0.839-***********************
  +0.657-**********************************************************************
  +0.514-***********************
  +0.402-******************
  +0.315-****************
  +0.247-**********
  +0.193-*********
  +0.151-*******
  +0.118-****
 +0.0926-**
 +0.0725-***
 +0.0567-**
 +0.0444-**
 +0.0347-**
 +0.0272-***
 +0.0213-***
 +0.0167-***
 +0.0130-****
 +0.0102-****
+0.00799-***
 0.00626-****
 0.00450-******
+0.00363-*****
 0.00300-*
```

```
                      MICROMERITICS AUTO-PORE 9200 V2.02                       PAGE 6

ONTARIO RESEARCH FPL                                               LP 16:58:22 4/18/85
#104    SHALE CLAY CEO2                                            HP 17:20:3 4/18/85
NTR NUMBER    +37

                      INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.152087E-001

         0%           20%          40%          60%          80%          100%
         I............I............I............I............I............I
    +300-*
    +235-*
    +184-*
    +144-****
    +113-******
   +88.1-*******
   +69.0-*******
   +54.0-*****
   +42.3-***
   +33.1-***
   +25.9-**
   +20.3-**
   +15.9-***
   +12.4-***
   +9.72-*****
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-**
   +2.86-****
   +2.24-******
   +1.75-*******
   +1.37-**********
   +1.07-**************
  +0.839-**********************************************
  +0.657-******************************************************************
  +0.514-******************
  +0.402-**************
  +0.315-*************
  +0.247-********
  +0.193-********
  +0.151-*******
  +0.118-***
 +0.0926-**
 +0.0725-***
 +0.0567-**
 +0.0444-***
 +0.0347-**
 +0.0272-**
 +0.0213-**
 +0.0167-**
 +0.0130-***
 +0.0102-***
+0.00799-***
+0.00626-****
+0.00490-******
+0.00383-*****
+0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                    PAGE 6

NTARIO RESEARCH FPL                                           LP 11:27:52 4/18/85
104    SHALE CA(OH)2                                          HP 14:31:54 4/18/85
NTR NUMBER     +6

                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.167742E-001

         0%          20%           40%           60%           80%           100
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-***
    +113-*****
   +88.1-********
   +69.0-*****
   +54.0-****
   +42.3-****
   +33.1-***
   +25.9-***
   +20.3-***
   +15.9-**
   +12.4-***
   +9.72-**
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-***
   +2.24-********
   +1.75-*************
   +1.37-**********************
   +1.07-******************************************
  +0.839-**********************************************************************
  +0.657-***********************************************************
  +0.514-************
  +0.402-*******
  +0.315-*******
  +0.247-******
  +0.193-*****
  +0.151-****
  +0.118-***
 +0.0926-*
 +0.0725-***
 +0.0567-**
 +0.0444-***
 +0.0347-*
 +0.0272-**
 +0.0213-**
 +0.0167-**
 +0.0130-****
 +0.0102-******
+0.00799-******
 0.00626-******
 0.00490-*********
+0.00383-*********
 0.00300-*
```

```
                  MICROMERITICS AUTO-PORE 9200 V2.02                   PAGE 6

ONTARIO RESEARCH FPL                                       LP 9:0:20 4/17/85
104     SHALE CLAY  LIGNOSOL                               HP 9:30:0 4/17/85
PNTR NUMBER    +6

                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                             100% = +0.172753E-001

          0%          20%           40%           60%           80%          100
          I............I.............I.............I.............I.............I
     +300-*
     +235-*
     +184-*
     +144-*
     +113-**
    +88.1-***
    +69.0-**
    +54.0-**
    +42.3-*
    +33.1-*
    +25.9-*
    +20.3-*
    +15.9-*
    +12.4-*
    +9.72-*
    +7.61-*
    +5.96-*
    +4.66-*
    +3.65-**
    +2.86-***
    +2.24-*****
    +1.75-******
    +1.37-*********
    +1.07-*************
   +0.839-*****************************************************
   +0.657-****************************************************************************
   +0.514-***
   +0.402-*
   +0.315-*
   +0.247-*
   +0.193-*
   +0.151-*
   +0.118-*
  +0.0926-*
  +0.0725-*
  +0.0567-*
  +0.0444-*
  +0.0347-*
  +0.0272-*
  +0.0213-*
  +0.0167-*
  +0.0130-*
  +0.0102-*
 +0.00799-*
  0.00626-*
  0.00490-*
 +0.00383-*
 +0.00300-*
```

```
                  MICROMERITICS AUTO-PORE 9200 V2.02                  PAGE 6

ONTARIO RESEARCH FPL                                       LP 14:29:19 4/17/85
 04    SHALE CLAY BACO3                                    HP 15:0:0 4/17/85
 NTR NUMBER    +6


                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.261245E-001

         0%          20%           40%           60%           80%          100%
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-**
    +113-***
   +88.1-****
   +69.0-***
   +54.0-**
   +42.3-**
   +33.1-**
   +25.9-*
   +20.3-*
   +15.5-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-**
   +1.37-***
   +1.07-***
  +0.839-****************
  +0.657-**********************************************************************
  +0.514-************************
  +0.402-***************
  +0.315-**************
  +0.247-********
  +0.193-*******
  +0.151-*****
  +0.118-***
 +0.0926-*
 +0.0725-***
 +0.0567-*
 +0.0444-*
 +0.0347-**
 +0.0272-**
 +0.0213-**
 +0.0167-*
 +0.0130-**
 +0.0102-**
+0.00799-***
 0.00626-***
 0.00490-***
+0.00383-**
+0.00300-*
```

```
                          MICROMERITICS AUTO-PORE 9200 V2.02                     PAGE 6

        ONTARIO RESEARCH FPL                                            LP 14:29:19 4/17/85
         104    SHALE CLAY SRC03                                        HP 15:0:0 4/17/85
         NTR NUMBER    +15

                           INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                           100% = +0.242332E-001

                  0%           20%           40%           60%           80%          100%
                  I.............I.............I.............I.............I.............I
             +300-*
             +235-*
             +184-*
             +144-*
             +113-*
            +88.1-**
            +69.0-**
            +54.0-*
            +42.3-*
            +33.1-*
            +25.9-*
            +20.3-*
            +15.9-*
            +12.4-*
            +9.72-*
            +7.61-*
            +5.96-*
            +4.66-*
            +3.65-*
            +2.86-*
            +2.24-*
            +1.75-**
            +1.37-****
            +1.07-******
           +0.839-*************************
           +0.657-***********************************************************************
           +0.514-**********************
           +0.402-***************
           +0.315-**************
           +0.247-********
           +0.193-*******
           +0.151-*****
           +0.118-***
          +0.0926-**
          +0.0725-***
          +0.0567-**
          +0.0444-**
          +0.0347-**
          +0.0272-**
          +0.0213-**
          +0.0167-**
          +0.0130-**
          +0.0102-***
         +0.00799-***
         +0.00626-****
         +0.00490-******
         +0.00383-*****
         +0.00300-*
```

```
                  MICROMERITICS AUTO-PORE 9200 V2.02                    PAGE 6

 NTARIO RESEARCH FPL                                       LP 11:27:52 4/18/85
 #107    [illegible] CLAY CA(OH)2                          HP 14:31:54 4/18/85
 NTR NUMBER   +15

                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.138698E-001

         0%          20%           40%           60%           80%           100%
         I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-***
    +113-*****
   +88.1-*******
   +69.0-****
   +54.0-**
   +42.3-**
   +33.1-***
   +25.9-****
   +20.3-***
   +15.9-****
   +12.4-*****
   +9.72-****
   +7.61-**
   +5.96-*
   +4.66-*
   +3.65-*****
   +2.86-*******
   +2.24-************
   +1.75-************
   +1.37-*********************
   +1.07-***************************************
  +0.835-**********************************************************************
  +0.657-****************************************************************
  +0.514-**************
  +0.402-*********
  +0.315-*********
  +0.247-*****
  +0.193-*****
  +0.151-*****
  +0.118-***
 +0.0926-***
 +0.0725-***
 +0.0567-*****
 +0.0444-****
 +0.0347-****
 +0.0272-******
 +0.0213-*****
 +0.0167-****
 +0.0130-******
 +0.0102-********
 0.00799-********
+0.00626-**********
 0.00490-**************
 0.00383-*****************
 0.00300-*
```

```
                        MICROMERITICS AUTO-PORE 9200 V2.02                  PAGE 6

NTARIO RESEARCH FPL.                                            LP 11:32:27 4/16/85
07        CLAY LIGNOSOL                                         HP 11:54:49 4/16/85
PNTR NUMBER    +21

                        INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                      100% = +0.109736E-001

             0%           20%           40%           60%           80%           100
             I.............I.............I.............I.............I.............I
     +300-*
     +235-*
     +184-*
     +144-**
     +113-***
    +88.1-****
    +69.0-***
    +54.0-***
    +42.3-***
    +33.1-***
    +25.9-***
    +20.3-*****
    +15.9-*****
    +12.4-******
    +9.72-******
    +7.61-***
    +5.96-*
    +4.66-***
    +3.65-********
    +2.86-********
    +2.24-***********
    +1.75-***********
    +1.37-*****************
    +1.07-******************************
   +0.839-************************************************************************
   +0.657-*************************************************************
   +0.514-*****************
   +0.402-************
   +0.315-*********
   +0.247-**
   +0.193-*
   +0.151-*
   +0.118-*
  +0.0926-*
  +0.0725-*
  +0.0567-*
  +0.0444-*
  +0.0347-*
  +0.0272-*
  +0.0213-*
  +0.0167-*
  +0.0130-*
  +0.0102-*
 +0.00799-*
  0.00626-*
  0.00490-*
 +0.00383-*
  0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                   PAGE 6

ONTARIO RESEARCH FPL                                          LP 11:32:27 4/16/85
 07          CLAY SRC03                                       HP 11:54:49 4/16/85
 NTR NUMBER    +37


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                   100% = +0.130706E-001

         0%           20%           40%           60%           80%          100%
         I............I.............I.............I.............I............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-**
   +88.1-***
   +69.0-**
   +54.0-**
   +42.3-**
   +33.1-**
   +25.9-**
   +20.3-**
   +15.9-****
   +12.4-******
   +9.72-*****
   +7.61-***
   +5.96-*
   +4.66-**
   +3.65-*****
   +2.86-*****
   +2.24-*******
   +1.75-*******
   +1.37-*********
   +1.07-****************
  +0.839-***************************************************************
  +0.657-*********************************************************************
  +0.514-**
  +0.402-*
  +0.315-*
  +0.247-*
  +0.193-*
  +0.151-*
  +0.118-*
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
+0.00799-*
 0.00626-*
 0.00490-*
+0.00383-*
 0.00300-*
```

```
                              MICROMERITICS AUTO-PORE 9200 V2.02                    PAGE 6

ONTARIO RESEARCH FPL                                                  LP 11:32:27 4/16/85
 07           CLAY BLANK                                              HP 14:49:10 4/16/85
 TR NUMBER    +23

                         INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                      100% = +0.979117E-002

                0%          20%           40%           60%           80%          100%
                I............I.............I.............I.............I.............I
           +300-*
           +235-*
           +184-*
           +144-**
           +113-****
          +88.1-*****
          +69.0-***
          +54.0-***
          +42.3-******
          +33.1-******
          +25.9-*****
          +20.3-*********
          +15.9-***************
          +12.4-*********
          +9.72-********
          +7.61-****
          +5.96-*
          +4.66-**
          +3.65-*******
          +2.86-********
          +2.24-***********
          +1.75-**********
          +1.37-***************
          +1.07-************************
         +0.839-****************************************************************
         +0.657-**********************************************************************
         +0.514-*******************
         +0.402-**************
         +0.315-***************
         +0.247-*********
         +0.193-*********
         +0.151-********
         +0.116-****
        +0.0926-***
        +0.0725-*****
        +0.0567-***
        +0.0444-****
        +0.0347-**
        +0.0272-***
        +0.0213-**
        +0.0167-*
        +0.0130-**
        +0.0102-***
       +0.00799-***
       +0.00626-**
       +0.00490-**
       +0.00363-**
       +0.00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                         PAGE 6

ONTARIO RESEARCH FPL                                                    LP 11:32:27 4/16/85
 #107     . CLAY CE02                                                   HP 14:49:10 4/16/85
NTR NUMBER    +40


                      INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                           100% = +0.123723E-001

        0%           20%           40%           60%           80%           100%
        I............I.............I.............I.............I.............I
   +300-*
   +235-*
   +184-*
   +144-*
   +113-*
  +86.1-**
  +69.0-**
  +54.0-*
  +42.3-*
  +33.1-*
  +25.9-*
  +20.3-*
  +15.9-*
  +12.4-*
  +9.72-*
  +7.61-*
  +5.96-*
  +4.66-*
  +3.65-*
  +2.86-****
  +2.24-******
  +1.75-********
  +1.37-************
  +1.07-*******************
 +0.839-*************************************************************
 +0.657-**********************************************************************
 +0.514-*******************
 +0.402-***************
 +0.315-***************
 +0.247-**********
 +0.193-***********
 +0.151-**********
 +0.118-******
+0.0926-****
+0.0725-******
+0.0567-****
+0.0444-*****
+0.0347-***
+0.0272-****
+0.0213-***
+0.0167-**
+0.0130-**
+0.0102-**
+0.00799-**
+0.00626-*
0.00490-***
0.00383-**
+0.00300-*
```

```
                     MICROMERITICS AUTO-PORE 9200 V2.02                    PAGE 6


ONTARIO RESEARCH FPL                                               LP 9:0:20 4/17/85
 07       --  CLAY BA2CO3                                          HP 9:30:0 4/17/85
PNTR NUMBER    +15


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                              100% = +0.142462E-001

              0%          20%           40%          60%          80%          100%
              I............I............I............I............I............I
    +300-*
    +235-*
    +184-*
    +144-**
    +113-***
   +68.1-***
   +65.0-**
   +54.0-**
   +42.3-*
   +33.1-**
   +25.9-*
   +20.3-**
   +15.9-**
   +12.4-***
   +9.72-***
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*****
   +2.86-******
   +2.24-*******
   +1.75-*******
   +1.37-********
   +1.07-***********
  +0.839-***********************************************
  +0.657-*********************************************************************
  +0.514-*********************
  +0.402-**************
  +0.315-****************
  +0.247-*********
  +0.193-*****
  +0.151-**
  +0.116-*
 +0.0926-*
 +0.0725-*
 +0.0567-*
 +0.0444-*
 +0.0347-*
 +0.0272-*
 +0.0213-*
 +0.0167-*
 +0.0130-*
 +0.0102-*
+0.00799-*
+0.00626-*
+0.00490-*
+0.00383-*
+0.00300-*
```

POOR
QUALITY
ORIGINAL